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CXVIII. *On the Nature and Origin of the Earth's Surface Structure.* By J. JOLY, *F.R.S.*, and J. H. J. POOLE, *Sc.D.**

WITHIN recent years seismic evidence has been frequently evoked as a means of elucidating the structure and physical state of the outer parts of the earth.

The recent analysis by Dr. Harold Jeffreys ('Nature,' vol. 118. Sept. 25th, 1926) of seismic data obtained on the occasion of the Kulpa Valley earthquake of 1909, the Wurtemberg earthquake of 1911, the Tauern earthquake of 1923, and the Oppau explosion, indicate a continental layer of from 20 to 30 km. in thickness and possessing a density the same as that of granite. Beneath this, the rate of transmission of compressional waves indicates a layer of higher density and possessing a thickness of about 20 km. The velocity of compressional waves in this layer suggests that it may consist of basaltic glass. Beneath this is a layer having a density agreeing with that of dunite (3·3) and which extends downwards to a depth of 1200 km. The inferences respecting density are based upon the experimental work of E. D. Williamson and L. H. Adams † upon the velocity of compressional waves in granite, and of L. H. Adams and R. E. Gibson ‡ who extended similar

* Communicated by the Authors.

† Journ. Franklin Inst. April 1923.

‡ Proc. Nat. Acad. Sci. May 1926.

measurements to basaltic glass and dunite at ordinary temperatures and at pressures corresponding to depths of about 30 km. Dr. Jeffreys in his deductions based on these experiments makes some allowance for the higher temperatures within the crust.

Dr. Jeffreys is quite explicit respecting the degree of uncertainty attending the seismic evidence. "The results," he says, "indicate very definitely that there is an upper layer that transmits compressional waves with a velocity of 5·6 km./sec. (though a velocity of 5·4 km./sec. would fit the Oppau explosion slightly better) and a lower one where the velocity is 7·8 km./sec. In addition, the Tauern earthquake gave rise to a wave with a velocity of 6·2 km./sec. which must have travelled in an intermediate layer. The probable error of all these velocities does not exceed 0·1 km./sec." After a review of the various sources of possible error, he concludes :—"I think, therefore, that determinations of the depths of the layers by means of near earthquakes are not more reliable than those based on the earth's thermal state, isostatic balance between continents and oceans, and the group-velocities of surface waves. All these are affected by uncertainty concerning the thickness of the basaltic layer, but the uncertainties of the method based on the compressional waves from near earthquakes appear more serious. The results taken as a whole are as consistent as can be expected : a thickness of 10 to 15 km. for each layer would be within the range of uncertainty of every method."

To these remarks must be added the criticism that the existence of basaltic glass in regions below the continents involves very rapid cooling after fusion. But rapid chilling at these depths is clearly impossible. The very same magma poured out at the surface of the continents and cooled under atmospheric conditions reveals to us in the plateau basalts a thoroughly crystalline constitution. If we assume the existence of temperatures above the crystallizing-point—which is quite probable—we must discard the extraordinary distribution of temperature downwards which has been deduced from the experiments referred to above, *e. g.* a temperature of 850° at a depth of 48 km. ('Nature,' May 15th, 1926.)

On seismic evidence Oldham deduced 30 km. as the depth to which continental materials extended. Wierchert traced these materials to a depth of 35 km.

In support of the view that a basaltic substratum underlies the continents there is, additional to the seismic evidence,

strong evidence arising out of certain events of surface history. At intervals extending back to the Archæan, great floods of molten basalt have been poured out at the earth's surface. The evidence is strong that these floods emerged at a temperature above the normal melting-point. They flowed for many miles before their progress was arrested by congelation, and today exhibit a horizontality of surface which indicates almost perfect fluidity. Washington * would ascribe this remarkable fluidity to the fact of the high percentage of iron to be found in these basalts ; but Daly, Prestwich, and many other authorities refer it to superheating of the emergent basalt arising out of the fall in pressure. This clearly points to a deep-seated origin †.

Further and very strong evidence for the world-wide distribution of basaltic magma beneath the continents arises out of the discovery by Washington that the chemical and mineral composition of the "plateau" basalts are strikingly alike although poured out over widely-sundered regions. He deals with five such regions : The Deccan ; Oregonian ; Thulean (Hebridean) ; Patagonian ; and New Jersey (*loc. cit.* p. 765 *et seq.*). Dealing with the first three of these, we have found a similarity in the amounts of parent radioactive elements, uranium and thorium, equally remarkable—as will presently be referred to.

The Continental Layer.

The evidence arising out of isostasy for the mean thickness of the continental layer appears to us to be the most direct available. A brief statement of it will suffice. We accept the geodetic data showing that the average elevation of the continental surface above the ocean floor is 4·62 km., and assume that this floor is the surface of the substratum. The mean depth of the oceans is 3·8 km. The buoyant effect of the ocean water upon the continents must be allowed for. This reduces the emergent part of the continents effectively to 3·22 km. If we assume that the known relative density of granite and basalt prevails fairly constant throughout the entire depth where the one is immersed in the other and that 2·67/3·00 expresses this ratio, it is easy to show that the

* Bull. Geol. Soc. Am. vol. xxxiii. p. 803 (Nov. 1922).

† Daly, 'Igneous Rocks and their Origin,' p. 459. See also Prestwich's 'Geology,' vol. i. p. 391 ; J. C. Russell's 'North America,' 1904, p. 322 ; Wadia's 'Geology of India,' p. 192 *et seq.*

support of 3·22 km. of emergent granite involves a submergence of about 25·8 km. Adding the emergent height, we arrive at an average continental thickness of 30·4 km.*

Wherein is this result assailable? The seismic data appear to show that the media concerned—*i. e.* the granitic and basaltic—retain their physical properties in the depths sufficiently, at least, to justify the underlying assumption of the argument.

We shall next summarize the thermal evidence. The average rate at which heat is being emitted at the continental surface is, theoretically, determinable from the gradient of temperature downwards and the conductivity of the rocks. But owing to the variable character of both data, the result is of very uncertain value.

We take the density of average granite to be 2·67, and assume that such rocks compose the great bulk of the continents. As the result of many experiments, we ascribe to the uranium family of radioactive elements the evolution of heat at the rate of $44{\cdot}8 \times 10^{-14}$ cals. per sec. per c.c. ; to the thorium series $35{\cdot}2 \times 10^{-14}$ cals. per sec. per c.c. The experimental work so far available respecting the evolution of heat from potassium (Holmes and Lawson, Phil. Mag. Dec. 1926) unfortunately leaves some uncertainty as to the rate at which this element radiates energy. Accepting the estimate which Holmes and Lawson regard as most probable and which approximates to a major limit we find, in average granite, that this element develops $34{\cdot}9 \times 10^{-14}$ cals. per sec. per c.c. The total is 115×10^{-14} cals. per sec. per c.c. We assume that all this heat passes upwards, escaping at the continental surface.

Now if the continents possess an average thickness of 30 km., the total quantity which passes out per square centimetre per second is 345×10^{-8} calories. Taking the thermal conductivity of the surface materials *in situ* as 0·008, we find that the surface gradient should be 23·3 metres per degree. The average rise of temperature close to the surface is often taken as 30 m. per degree, but this is known to steepen downwards. Arrhenius cites the gradients observed in many artesian borings as varying from 19 to 38 metres per degree downwards, omitting one exceptional result †. When it is remembered that continental thickness must vary from one region to another and that the surface conductivity necessarily varies with the humidity, physical

* J. Joly, 'The Surface History of the Earth,' p. 35.
† 'Lehrbuch der Kosmischen Physik,' p. 280.

structure and nature of the rocks, we see that only approximate results are to be expected. A lesser continental depth than 30 km. would evidently be more in accord with the average surface gradient. The possibility that we are allowing too much for the thermal importance of potassium has to be kept in mind.

Yet another thermal effect has to be considered:—the basal continental temperature which may be assumed to arise out of the three factors: the continental depth, the radioactivity of the rocks, and their mean conductivity. The equation for this is

$$\theta = \frac{Q \times D^2}{2K},$$

where Q is the quantity of heat generated per second in one c.c. of the rocks as determined above; D is the depth in centimetres, and K is the conductivity. The latter value applies to dry granitic rock for which K may be taken as 0·004 or possibly 0·005. Inserting the value of Q as given above and assuming a continental depth of 30 km., we find $\theta = 1290°$. If K is taken as 0·005 the value of θ becomes 1035°.

Bridgeman has experimentally shown that the thermal conductivity of rocks increases, but only very slowly, with increased pressure. "For the ordinary rock of the earth's crust the effect is not over 0·5 per cent. per 1000 kilograms per square cm. at ordinary temperatures. The absolute conductivity and its pressure coefficient may either increase or decrease with rise of temperature" (Am. J. Sc. Feb. 1924). 1000 kilograms pressure per sq. cm. corresponds to a depth in the earth's crust of about 4 km. This effect would lower estimates of basal temperature, but not significantly. The basal temperature, using the lower value of K, is probably not too high to meet the pressure conditions, as these affect the melting-point of the substratum. As we have already seen, there is strong evidence that the plateau basalts flowed out at a temperature above the normal melting-point.

Upon the whole it would appear that a mean continental depth of 30 km. is in harmony with the geodetic measurements of mean continental elevation above the ocean floor and the isostatic conditions where the sustaining substance is basaltic in character. It appears to be the least depth—or nearly the least—which we can assume if we are to look for a basal temperature approximating to that of the melting-point of a basaltic substratum. We seem to get very little guidance

from surface gradients. But upon the whole they are rather in favour of a mean continental thickness somewhat less than 30 km.

The Basaltic Substratum.

We possess two sources of information respecting the chemical nature and radioactivity of the basaltic substratum.

The substratum must be regarded as reaching the surface, where it is covered by the ocean floor. Its covering of oceanic deposits can attain an average thickness of some 200 metres only *. We cannot reach the ocean floor, but it is a fair assumption that the basaltic islands attaining the surface of the ocean give us an indication of its nature—if not of its very uppermost levels, at least of levels but a relatively small distance downwards. They are necessarily derived from volcanic pockets at no great distance beneath and, from the frequently linear distribution of many of these islands, probably situated along fissures or cracks developed under the action of tensile forces. On the other hand, the plateau basalts give us information respecting the subcontinental basalt. The vertical difference between the two levels is considerable—some 26 km.

Washington has made chemical analyses of 72 rocks derived from the floor of the Atlantic and 56 analyses of rocks from the floor of the Pacific. They agree closely. The percentage of K_2O is 2·31 for the Atlantic rocks; 2·10 for the Pacific †. The percentage of ferrous oxide is low, that of alumina and silica tends to be high. The constituents suggest a rock of low density. The densities calculated on the analyses are in the mean 2·87. Later Washington deduced 2·91, using differing densities for the normative minerals. This mode of determining the mineral composition is objected to by many authorities, and we think with good reason ‡. The same magma may give rise to very different mineral structures with attendant differences of densities. The method, indeed, escapes the difficulties arising out of vesicularity, which can only be surmounted by very special care when densities are measured by immersion of the specimen in liquids of known specific gravity.

We have made determinations of the density of 12 basalts obtained from Honolulu, Cape Verde, Madeira, Island of Ascension, Kerguelen Island, St. Helena, Juan Fernandez, and

* 'Radioactivity and Geology,' 1909, p. 56 *et seq.*

† Bull. Geol. Soc. Am. vol. xxxiii. p. 388 (1922).

‡ Daly, *loc. cit.* pp. 9 *et seq.*

Fernando Noronha, using special precautions where there was any sign of vesicularity, and of course rejecting all specimens revealing secondary effects due to weathering etc., such as development of zeolites or other minerals forming in vesicles or cracks. The details will appear later. The 12 rocks afforded a mean density of 2·890.

The radioactivity of several island basalts are cited in a former paper *.

The means are as follows :—

	$Ra \times 10^{-12}$ grms. per grm.	$Th \times 10^{-5}$ grms. per grm.
Atlantic Islands	1·31	0·87
Indian Ocean Islands	0·86	0·65
Pacific Islands	1·09	0·32

The basalts from 12 different islands were examined, 17 separate samples being dealt with.

Grouping the islands of the Indian Ocean with those of the Pacific and adopting Washington's values for the percentages of K_2O in Atlantic and Pacific basalts and making use of factors previously cited, we deduce the following values for the rate of thermal evolution :—

	Calories per grm. per million years.
Atlantic Island Basalt.	
Uranium group	2·31
Thorium group	1·81
Potassium	2·38
Total.....	6·50
Pacific Island Basalt.	
Uranium group	1·74
Thorium group	0·91
Potassium	2·16
Total.....	4·81

For oceanic basalts, according to these measurements, the evolution of heat is in the mean at the rate of 5·65 calories per gram per million years.

This is the rate of thermal development in the upper parts of the substratum, and it would appear that the basalts crystallized out of this upper part of the substratum possess an average density of closely 2·890.

The next information we get as to the nature of the substratum is derived from the plateau basalts, which we

* Phil. Mag. Nov. 1924.

reasonably refer to the region which extends immediately beneath the continents. The chemical and mineral character of these rocks has been carefully studied by H. S. Washington *.

His tables deal with a total of 58 analyses from 5 important regions: the Deccan; the Oregonean (or Columbia River and Snake River basalts); the Thulean (or Hebridean); Patagonian; and New Jersey.

In these rocks, thin sections show a striking uniformity in mineral character (mode) or at least in general mineral composition. "Chemically they differ materially from other basalts,"—"in their much higher percentage of iron oxides with ferrous oxide greatly predominating,"—and in their higher titanium content. The excess of iron is less marked in the Triassic plateau basalts of New Jersey and in the Algonkian basalts of the Lake Superior region, but these are still abnormal in this respect. Washington considers the Deccan, Oregonian, and Thulean flows as the most typical of the plateau basalts. His results show that in these great flows—taking place in widely sundered regions of the globe—"the averages are closely alike." "In the typical plateau basalts the combined iron oxides would amount to about 14 per cent. or more, and this is the more remarkable if only the most abundant group of the femic basalts are considered."

Regarding the density of these basalts, we have examined three samples of authentic Oregonian rocks. They averaged 2·897. Five specimens of Thulean basalt, all fairly good, gave 2·912, and four very good samples of the Deccan flow gave 2·982. The mean of all twelve is 2·930. This is somewhat higher than the result obtained for the basalts derived from the oceanic islands—2·890. Although the difference is small, we believe it is real. The difference in the content of iron and titanium in the two classes of basalt as revealed by Washington's analyses would, in fact, involve an appreciable difference in density. Thus, for the oceanic basalts the mean percentage of Fe_2O_3 is 4·16 and of FeO it is 6·01. In the plateau basalts, $Fe_2O_3 = 3·47$ and $FeO = 9·35$. Again, TiO_2 in the oceanic basalts averages 1·79 per cent.; in the plateau basalts it averages 2·30. On the other hand, the content of alumina in oceanic basalts is 15·66 per cent.; in the plateau basalts it is 13·62. The silica content of the island basalts slightly predominates.

* "Deccan Traps and other Plateau Basalts," Bull. Geol. Soc. Am. xxxiii., 1922.

We have elsewhere cited results * on the radioactivity of the plateau basalts of the Deccan and of the Hebridean (Thulean) regions and also some on material of uncertain Oregonian origin. Thanks to the kindness of Prof. Daly and Prof. W. D. Smith and of Prof. H. Landes, we have been able to deal with 12 samples of undoubted Oregonian origin, one specimen being a part of one analysed by H. S. Washington.

The results are as follows for the three regions, the potassium content being estimated from the analyses cited by Washington (*loc. cit.*) :—

	Deccan (6).	Oregonian (12).	Thulean (6).
Radium, grams per gram.	$0{\cdot}77\times10^{-12}$	$0{\cdot}70\times10^{-12}$	$0{\cdot}77\times10^{-12}$
Thorium, „ „	$0{\cdot}46\times10^{-5}$	$0{\cdot}56\times10^{-5}$	$0{\cdot}49\times10^{-5}$
Potassium	$0{\cdot}59\times10^{-2}$	$1{\cdot}07\times10^{-2}$	$0{\cdot}83\times10^{-2}$

From these results, using data already cited, we find for the evolution of heat from average plateau basalt :—

From the Uranium series..... 1·32 cals. per gram in 10^6 years,
„ „ Thorium series..... 1·04 „ „ „
„ „ Potassium ..... 1·03 „ „ „

making a total of 3·39 calories per gram in one million years.

The thermal development progressing beneath the continents is, according to these results, very much slower than that which we have found for the upper parts of the substratum.

The Deeper Substratum.

The seismic evidence examined by H. Jeffreys indicated a downward extension of the basaltic substratum to the extent of some 20 km., after which there was a change of density ; a density comparable with that of dunite—3·3—succeeding and extending downward to a depth of 1200 km.

It becomes of interest to consider the chemical and radioactive properties of dunite. This rock belongs to the plutonic ultra-basic group. It is typically composed mainly of olivine. Chemically it is remarkable for its high percentage of magnesia (about 46 per cent.) and negligible content of alumina and lime. Its percentages of ferrous oxide and of silica compare with those of eclogite. But the eclogites contain from 9 to 17 per cent. of alumina, from 5 to 14 per cent. of lime, and about 17 per cent. of magnesia.

* Phil. Mag. Nov. 1924.

Radioactively there is not much difference between these rocks save in the fact that potassium is negligible or nil in dunites.

Two radioactive analyses for radium and thorium—one being carried out on the type rock from the Dun Mountains of New Zealand, the other from Krombal, Styria—gave closely concordant results (Phil. Mag. Nov. 1924, p. 829). The radium content in the mean was $0{\cdot}7 \times 10^{-12}$, and the mean thorium content was $0{\cdot}33 \times 10^{-5}$.

From these figures we find that the heat evolved is :

From the Uranium series	0·83	cals. per million years.
,, ,, Thorium series	0·69	,, ,, ,,
A total of	1·52	,, ,, ,,

The density of the type rock is given by Rosenbusch ('Elemente der Gesteinslehre,' p. 248) as 3·295.

There is considerable probability that not dunite but eclogite occupies the great depths.

We believe that Dr. L. L. Fermor was the first to infer the presence of eclogite in the deeper parts of the substratum *. He based his view upon the fact that eclogite is in reality heteromorphous with gabbro or basalt ; a form of basalt which will inevitably come into existence given certain pressure and temperature conditions: as when a basaltic magma crystallizes under such pressure conditions as must obtain far beneath the continents. Magmatically the rocks are identical, but mineralogically they are very different—the pressure having controlled the process of chemical combination in such a manner as to lead to the development of minerals possessing the maximum density: notably garnet. If carbon is present diamond will develop, as in the case of the diamond-bearing eclogites of S. Africa.

We have found that a typical eclogite, fused in the electric furnace, turns to a glass possessing the same density as glass derived from normal basalt, and quite indistinguishable from it. The parent eclogite possessed a density of 3·415, the glass a density of 2·746, which agrees with the density of diabase glass cited by Day, Sosman, and Hostetter †. The increase of volume is 24 per cent.

It is to be expected that experimental investigation on the compressibility of this rock will support its claims as the occupant of the great depths of the substratum. The density of eclogite varies from 3·2 to 3·5. That of dunite is 3·3.

* Journ. & Proc. Asiatic Soc. Bengal, vol. viii. p. 315 *et seq.* (Sept. 1912).

† Am. J. Sci. xxxvi. p. 331 (1913).

Obviously the simplifying assumption that the deeper parts of the substratum are heteromorphous respecting the higher parts and represent the downward extension of the same great basaltic magma which floats the continents, commends itself as probable.

This view confers considerable interest upon the chemical, radioactive, and physical characters of eclogite.

Eclogites are scarce rocks at the surface. They are found generally in lens-shaped masses contained in crystalline schists and gneisses; always associated with amphibolites, into which they appear to grade as the result of their instability at normal pressure. The change is purely internal or spontaneous, the bulk analysis revealing no chemical alteration *.

Fermor has suggested a plausible reason for the occasional appearance of these rocks at the surface. This would become possible if, owing to some abnormality of deep-seated temperature gradients, cooling forestalled, as it were, the effects of decreased pressure upon material being carried up to the surface. They would be, in fact, cooled before the diminution of pressure could bring about the destruction of the piezocrystalline structure of the rock. This appears to be more probable than the assumption that the piezocrystalline structure actually originated near the surface under specially intense dynamic conditions such as might prevail in tectonic areas.

If we are correct, as we believe, in our support of the views of Dr. Fermor, we seem justified in paying special attention to the properties of eclogite for, in fact, they may have controlled to a large extent the surface history of the earth.

Although there appeared to be no *a priori* reason to expect that these rocks would differ in their radioactive characters from the plateau basalts, a few experiments showed that the eclogites possess rather less than one-half the radium and thorium content of the plateau basalts. Extending our results we found the following averages:—Mean radium content of 17 eclogites from various localities, $0{\cdot}33 \times 10^{-12}$, grams per gram. Mean thorium content of the same rocks, $0{\cdot}18 \times 10^{-5}$ grams per gram. As regards the content of potassium, Rosenbusch cites 17 analyses, the mean content of K_2O being 0·707 per cent.† Mlle Brière‡ cites

* Mlle Y. Brière, "Les Eclogites françaises," *Bull. Soc. Française de Min.* tome xliii. p. 127.

† 'Elemente der Gesteinslehre,' 1923, p. 718. ‡ *Loc. cit.* p. 168.

11 analyses, the mean K_2O content being 0·37 per cent. Mlle Brière remarks upon this poverty of potash. The mean of both authorities is 0·57 per cent., from which we estimate the mean content of potassium as 0·44 per cent.

Using the data previously cited, we find for the eclogites the following rate of thermal genesis :—

For the Uranium group	0·58	cals. per gram per million years.
„ Thorium group	0·37	„ „ „ „
„ Potassium	0·54	„ „ „ „

The total for all is 1·49 cals. per gram per million years.

This is less than half the thermal output of the plateau basalts, *i. e.* 3·39 cals. per gram per million years ; while the island basalts, representing the topmost layer of the substratum, generate heat at the rate of 5·56 cals. per gram per million years. Finally the rocks of the continents generate 15·13 cals. per gram per million years.

Of hardly less interest is the density of these rocks. The density of 14 eclogites afforded a mean value of 3·376. This agrees with the data cited by Rosenbusch (*loc. cit.*) and by Mlle Brière (*loc. cit.*).

The following table contains the foregoing results :—

	Calories generated per gram per million years.	Density.
Continents.....	15·13	2·67
Suboceanic basalts	5·65	2·89
Sub-continental basalts.....	3·39	2·93
Dunite layer (?).....	1·52	3·29
Eclogite layer (?)	1·49	3·38

The physical properties displayed in this table must have influenced fundamentally the surface history of the globe. The question as to how such a remarkable stratification can have originated remains to be considered.

The Origin of the Earth's Surface Structure.

As the result of the foregoing data respecting the density and radioactivity of the earth's outer materials we find a gradation in density which *diminishes* upwards, attended by a gradation in radioactivity which *increases* upwards. It seems obvious that these reciprocal phenomena must have a physical and causative connexion. We find a simple explanation of the surface structure if we admit the existence

at some past time of a heterogeneous admixture of units possessing different degrees of radioactivity and different densities; every degree of radioactivity within limits and every degree of density within limits, affecting these units. These units may differ in magnitude. They may be supposed to be promiscuously intermixed. They are essentially composed of rock substances: *i. e.*, of oxides of certain abundant elements—silicon, aluminium, iron, magnesium, calcium, sodium, potassium—in various proportions; which proportions are independent of the amount of radioactive elements present.

A condition of what we may call uniform heterogeneity in such an admixture would not be stable in a gravitational field, and could not continue to exist. There would always be a tendency for the more radioactive and less dense units to migrate upwards and for the less radioactive and more dense units to move downwards. Again, consider a unit of average density possessing more of the heat-producing elements than the surrounding units. It accumulates heat more rapidly than the neighbouring units, increases proportionately in volume, and when fusion finally prevails in its surroundings it gravitates upwards. The same tendency is possessed by the more siliceous and aluminous units. On the other hand, a unit poor in radioactive elements retains a higher density than its surroundings and, when gravity is free to act upon it, from this cause alone it tends to sink downwards. So also the more ferruginous and the more titaniferous units seek the lower levels. The observed poverty of the denser rocks in radioactive elements and the richness of the lighter rocks in this way come about. We can, in fact, regard radioactivity as being gravitationally equivalent to the presence of elements of low density, and the conditions become simply those leading to ultimate gravitational separation according to density; the thermal effects of radioactivity conferring mobility. Hence heterogeneity is unstable, and the observed preferential association of the radioactive elements with rock-substances of low density involves no assumption of an unexplained affinity of radium, thorium, or potassium with silica or alumina.

Doubtless there is some return to heterogeneity on a large scale attending the events of a great revolution. But the instability must ultimately reassert itself, and there is an enormous time-interval during which segregation may progress. The slow accumulation of heat between the major revolutions probably occupies not less than 100 million years if we go on the assumption that the greater

revolutions involve the fusion of the deeper parts of the substratum *.

We may analyse to some extent the conditions arising in a heterogeneous substratum of the kind we are considering. Let D stand for a high density and d stand for low density and Δ for a mean or average density; similarly let T stand for a radioactively rich and t represent a radioactively poor unit, and τ one of average radioactivity. Then we have as gravitating upwards the combinations :

$$d+\mathrm{T} \quad d+\tau \quad \Delta+\mathrm{T},$$

and as gravitating downwards :

$$\mathrm{D}+t \quad \mathrm{D}+\tau \quad \Delta+t,$$

while the following retain a mean position :

$$d+t \quad \mathrm{D}+\mathrm{T} \quad \Delta+\tau.$$

The maximum acceleration upwards arises out of the combinations $d+\mathrm{T}$, and the maximum downwards out of $\mathrm{D}+t$.

Six out of the nine go up or down.

CXIX. *The Radioactivity of the Earth's Basaltic Magma.* By J. H. J. Poole, *Sc.D.*†

IN a previous paper written jointly with Professor Joly (Phil. Mag. vol. xlviii. Nov. 1924) on the radioactivity of the various basaltic outflows, it was pointed out that although the mean results for the Hebridean and the Deccan plateau basalts agreed very closely, still the figures obtained both for the radium and thorium content of the specimens of the Oregonian plateau basalt which we then possessed were on the average from two to three times greater. This fact was rather unexpected, since from the great similarity in chemical composition of all the plateau basalts, it is generally considered that they are all derived from the same sub-crustal basaltic magma, and that accordingly we would expect them to agree closely also in radioactivity. The simplest explanation we could offer at the time for this discrepancy, was that the real origin of the alleged Oregonian basalts was not very well established as they were merely purchased specimens. We therefore decided to repeat the determinations for the Oregonian basalts, as soon as specimens of undoubted authenticity could be obtained. Through the kindness of Professors R. A. Daly, Warren D. Smith, and Henry Landes,

* The Halley Lecture, 1924, pp. 131–35. A. Holmes, Geol. Mag. Nov. 1925.

† Communicated by Prof. J. Joly, D.Sc., F.R.S.

who have supplied us with the required material, we have now been enabled to carry out this intention, and the figures obtained are given in this paper. It is satisfactory to be able to state that the Oregonian basalt now comes completely into line with the other two plateau basalts previously examined. Apparently our previous specimens could not have been genuine Oregonian, and we desire to thank the donors of the new material for the trouble they have taken in the matter.

We have also carried out a series of determinations on various eclogites, a class of rock which has, as far as we know, not been dealt with before. The eclogites are a very interesting type of rock, since they only differ from ordinary basalt in mineral constitution and density, their gross chemical composition being practically identical with that of a basalt. It is generally assumed that they are simply a form of basalt which has solidified under very great pressure, which would naturally tend to favour the formation of the denser minerals and thus explain the higher density of the eclogite. This view is also favoured by the association of eclogites with diamonds in South Africa. If this hypothesis is correct, we should be justified in assuming that the eclogites really represented the lower layers of the Earth's basaltic magma; their radioactive properties certainly favour this conclusion since it will be seen that both their radium and thorium contents are much less than even those of the plateau basalts. The bearing of this result on the general views of the Earth's surface structure is being discussed elsewhere, and it would be superfluous to discuss it further here.

The radium contents were determined by the electric method. This method has been fully described in previous papers (Phil. Mag., July 1911, Oct. 1912, and July 1924). The mixed carbonates and boracic acid, used in the decomposition of the rock powder, were always de-emanated immediately before the experiment, by solution in water, and then evaporation of the solution to dryness. This plan entirely eliminates any error due to possible radioactive impurities in these chemicals, and was adopted in some of the later determinations given in the previous paper (*loc. cit.*). It is especially necessary to adopt this precaution in dealing with such very inactive rocks as eclogites. It may be noted that it is impossible to eliminate the radioactivity of the chemicals in a similar easy manner if the solution-method for determining the radium content is employed. Fortunately, in the thorium measurements where a solution-method must be used, no thorium can be detected in the carbonates and boracic acid.

The same electroscope as before was used, but as it had in the interim been fitted with a new gold-leaf, its constant was re-determined. The value obtained was $0{\cdot}8 \times 10^{-12}$ grm. of radium per scale division per hour, which agrees with the higher values obtained in the previous series of standardizations. This figure has accordingly been adopted in calculating all the results given in the following tables.

Some slight alterations were introduced into the practical details of the apparatus used in the thorium determinations. Thus an electric hot-plate was substituted for the ring gas-burner previously used for keeping the rock solution boiling, as it was found that variations in the gas pressure made it very difficult in keeping the solution boiling at a reasonably steady rate, and it was feared that variations in the rate of boiling might possibly affect the escape of the thorium emanation from the solution. In this respect the electrical heater effected a complete cure, as would naturally be expected. The plan adopted for drawing a constant current of air through the system was also slightly modified. Previously, a filter pump, worked from a constant pressure supply, was used to draw the air current through a small capillary air-leak. In this series of experiments a Gaede mercury pump driven by a constant speed electric motor through suitable reduction gearings was employed, as it was felt that perhaps a more truly constant air current might be obtained by this method. The rate of the pump was adjusted to give practically the same rate of flow as previously. The same electroscope, as previously, was made use of, and on re-standardization with a new thorianite standard solution, it gave practically the same value for the constant, showing that the speed of the air current must be practically the same as before. The actual rate of the current, as measured with a gasometer, was about 4 c.c. per sec., which is the same as the rate previously employed. For further details of the method the original papers should be consulted (Phil. Mag., May 1909, April 1915, and Nov. 1924).

In the course of this work on the basalts and eclogites, the general connexion between the radioactivity of a rock and its density was very apparent. Thus the eclogites, which only differ from basalt in density, are, as it will be seen, much less active. To investigate this point more clearly, the density of all suitable specimens, neglecting those which have undergone obvious alteration by weathering, etc., were determined. In some cases, more especially for surface basalts, the vesicularity of the basalts made it rather difficult to obtain the density of the rock directly. Under

these circumstances, the value for the rock when coarsely powdered was determined. In order to get rid of any air bubbles still included in the powder, the powder, while immersed in water, was placed under the receiver of an air-pump and exhausted. For convenience in reference in the following tables, the values for the plateau and island basalt previously published are included together with their densities as now determined.

The radium content is given in 10^{-12} g. per g., and the thorium in 10^{-5} g. per g. The densities are in g. per c.c.

We desire to express our thanks to the Trustees of the British Museum for the gift of some of the specimens of eclogite we have used.

ECLOGITES.

Locality.	Radium Content.	Thorium Content.	Density.
Specimen, T.C.D. Museum, Loc.?	0·57	0·35	3·417
Eppenreuth, Bavaria, British Museum No. 52738.	0·15	0·25	3·210
Nilgiri Hills, Madras, British Museum No. 757.	0·12	0·50	3·689
Fichtelgebirge, Bavaria, British Museum No. 12149.	0·75	0·27	3·365
Roberts Victor Mine, Orange Free State .	0·36	0·00	3·450
Eppenreuth, Bavaria.....	0·21	0·30	3·390
Silberbach, Fichtelgebirge	0·30	0·12	3·336
Stammbach, Fichtelgebirge, Bavaria	0·50	0·00	3·377
Marienbad, Bohemia.....	0·00	0·25	—
Lengefeld, Erzgebirge	0·31	0·19	3·205
Saasthal, Switzerland	0·42	0·03	—
Weissensteim, Fichtelgebirge	0·41	0·00	3·402
Fattigau, Oberfranken	0·17	0·50	3·424
Mollinezzo, Tessinfluss, Switzerland	0·16	0·00	3·242
Mochie, Saasthal, Switzerland	0·53	0·10	3·451
Kleinitz, Tirol	0·30	0·00	3·308
Polikan, Kuttenberg, Bohemia	0·41	0·17	—
Mean Value.....	0·33	0·18	3·376

Plateau Basalts.

Oregonian.

Locality.	Radium Content.	Thorium Content.	Density.
Columbia River Basalt, summit of Steen's Mt.	0·80	0·50	—
Ditto, Steen's Mt., 600 ft. below summit.	0·50	0·60	—
Ditto, Steen's Mt., flow 1050 ft. below summit.	0·60	0·55	—
Ditto, Steen's Mt., Dike 1000 to 1050 ft. below summit.	0·70	0·65	—
Ditto, Albert Rim, Lake county	0·50	0·45	—
Ditto, „ „ „ „	0·74	0·70	—
Ditto, „ „ N. side of Pine Creek.	0·90	0·70	—
Ditto, top flow, western wall of Grand Canyon.	0·70	0·57	—
Snake River, Idaho Falls.....	0·68	0·50	3·002
Steen Mountain	0·70	0·40	2·885
Snake River Canyon	0·90	0·57	2·805
Columbia Highway west of Hood River...	0·64	0·61	—
Mean Value.....	0·70	0·57	2·897

Deccan.

Locality.	Radium Content.	Thorium Content.	Density.
Index No. 20/861 Kasara-Igatpure	0·91	0·62	2·932
„ „ 20/855 Bombay, Nagpur Ry..	0·75	0·43	—
„ „ 20/851	0·60	0·37	3·010
„ „ 20/853	0·80	0·52	3·025
„ „ 20/850	0·82	0·56	2·959
„ „ 20/852	0·72	0·24	—
Mean Value.....	0·77	0·46	2·982

Hebridean.

Locality.	Radium Content.	Thorium Content.	Density.
Basaltic Lava, Iceland, nr. Hafna Jordun.	0·65	0·50	—
Vesicular Basalt, Iceland	1·00	0·45	—
Staffa	0·96	0·90	2·908
Tobermory, Mull	0·96	0·60	2·978
Blackhead, Co. Antrim	0·56	0·34	—
Giant's Causeway, Co. Antrim	0·50	0·17	2·891
Calve Island	—	—	2·964
Rathlin Island	—	—	2·818
Mean Value	0·77	0·49	2·912

Island Basalts.

Atlantic Islands.

Locality.	Radium Content.	Thorium Content.	Density.
Lava, St. Helena	1·81	1·0	—
Basalt, St. Helena	0·93	0·62	2·938
Ditto	—	—	2·940
Basalt, Ascension	0·76	0·43	2·870
Ditto	0·97	—	—
Olivine Basalt, Madeira	1·38	1·07	2·894
Basalt, Teneriffe, Canary Islands	2·77	1·78	—
Basalt, Flores, Azores	1·40	0·84	—
Olivine Basalt, Fernando Noronha	1·20	0·56	3·070
Ditto ditto	1·04	—	—
Basalt, Cape Verde Islands	0·86	0·64	3·010
Mean Value	1·31	0·87	2·954

Locality.	Radium Content.	Thorium Content.	Density.
Christmas Island	1·05	0·94	—
Island of Rodriguez	0·76	0·56	—
Kerguelen Island	0·77	0·45	2·922
Lava, Hawaiian Islands	1·25	0·28	—
Basalt, Hawaiian Islands	1·10	0·37	—
Lava, Kilauea	0·96	0·30	—
Juan Fernandez	1·06	0·32	2·939
Oahu, Palmer's Collection No. 2	—	—	2·711
Ditto No. 18	—	—	2·761
Ditto No. 4	—	—	2·661
Honolulu No. 17	—	—	2·967
Mean Value	0·99	0·46	2·827

The general means for the various basaltic materials are as follows :—

	Radium.	Thorium.	Density.
Eclogites	0·33	0·18	3·376
Plateau Basalts	0·75	0·51	2·932
Island Basalts	1·15	0·66	2·890

CXX. *An X-ray Examination of the Lower ω-Phenyl Normal Saturated Fatty Acids.* *By* A. L. Patterson, *M.Sc., A.Inst.P.* *

1. Introduction.

In the course of a general study of crystals of organic substances having one or more benzene nuclei in the molecule, benzoic acid (C_6H_5COOH) has been investigated by Sir W. H. Bragg †. In connexion with this work, it was thought interesting to study the homologous series of which benzoic acid is the first in order to find out what similarities,

* Communicated by Sir W. H. Bragg, K.B.E., F.R.S.

† Sir W. H. Bragg, Journ. Chem. Soc. cxxi. p. 2767 (1922).

if any, existed between the structures of benzoic acid and of the other members of the series whose general structural formula is

Of these substances, β-phenylpropionic acid has been investigated by Becker and Jancke *, who made use of the powder method.

In the present paper the results of an investigation of the first four members of the series are given †. The rotating-crystal method was used throughout, with the assistance of oscillation and Laue photographs and, in one instance, of ionization spectrometer measurements. The photographs were all taken using a Shearer-type tube with an iron anti-cathode. The graphical method of Bernal ‡ was used in the interpretation of the photographs. The substances, which were purified by recrystallization from petroleum ether, were prepared in the Laboratory by Mr. W. B. Saville.

2. Experimental Results.

(i.) *Phenylacetic acid* ($n=1$).—The crystallographic data for phenylacetic acid are very scanty. The observations of Haushofer §, as quoted by v. Groth ‖, are as follows:—The acid crystallizes in rhombic plates {100} with an angle 51° 30′. It has positive double refraction, the plane of the optical axes is (010), the first median line lies in the "*a*" axis, and the optical axial angle is small. Observations with a polarizing microscope confirmed these results.

Thin flakes were grown from petroleum ether. One or two thicker, but imperfect, crystals were grown from benzene and from formic acid. It was not possible to observe the faces which bounded the flake. On the basis of the unit cell given below, they belong to the zones [011] and [01$\bar{1}$], possibly the form {011} itself.

Rotation photographs taken about the "*b*" and "*c*" axes gave the values $b=4{\cdot}90$ Å. and $c=10{\cdot}10$ Å. A Laue photograph taken perpendicular to the flake (100) showed no

* Becker & Jancke, *Zeits. für phys. Chem.* xcix. p. 261 (1921).

† The names of these acids are: $n=1$, phenylacetic acid; $n=2$, β-phenylpropionic acid; $n=3$, γ-phenylbutyric acid; $n=4$, δ-phenylvaleric acid.

‡ Bernal, Proc. Roy. Soc. A, cxiii. p. 117 (1926).

§ Haushofer, *Zeits. für Krist.* ix. p. 525 (1884),

‖ v. Groth, *Chemische Kristallographie*, iv. p. 556. N.B.—The "*a*" and "*c*" axes have here been interchanged.

signs of the orthorhombic symmetry which Haushofer was led to expect from the optical properties *. This photograph gave a value for the monoclinic angle $\beta = 101°$. The measurement of the (100) plane which appeared on the equator in the "*b*" and "*c*" axis photographs gave a value $d_{100} = 13{\cdot}9$ Å. A rotation about the normal to the (100) face indicated that this corresponded to the full translation of the lattice. The indexing of the rotation and Laue photographs was carried out on this assumption, and no spots were observed which disagreed with this cell. The probable unit cell is, then,

$$a = 14{\cdot}2 \text{ Å.}, \quad b = 4{\cdot}90 \text{ Å.}, \quad c = 10{\cdot}1 \text{ Å.}, \quad \beta = 101°.$$

There are four molecules, $C_6H_5CH_2COOH$, in this cell. The rotation photograph about the "*a*" axis required to settle this cell finally was not obtained owing to the extreme flakiness of the crystals.

Only a few planes could be identified without ambiguity among the many which occurred on the rotation photographs. Their indices are given in Table I. Those planes which were identified as reflecting only in the first order in the Laue photograph are also given.

TABLE I.

$C_6H_5CH_2COOH$.

"*b*" axis.	"*c*" axis.	"*a*" face normal.	Laue.
100	100	002	$10\bar{2}$ (s.)
200	200	102	120 (v.w.)
110	300	$30\bar{2}$	126 (w.)
011	400	310	012 (s.)
$1\bar{1}1$	012	410	$21\bar{4}$ (w.)
210		$1\bar{1}1$	$52\bar{6}$ (m.)
		$31\bar{1}$	$54\bar{4}$ (w.)
			$72\bar{6}$ (v. w.)
			$11\bar{2}$ (s)

The absence of planes of the type (*ho*1) and (*ho*3) was particularly noticeable in the rotation about the normal to (100) face, and in that about the "*c*" axis. No trace of the reflexion (010) was found. The space-group which would agree with these conditions is $C_{2h}^5(b)$ †, in which the halved spacings are (010) and (*hol*) when *l* is odd.

* Haushofer, *loc. cit.*

† Astbury & Yardley, Phil. Trans. Roy. Soc. A, ccxxiv. p. 221 (1924).

(ii.) *β-phenylpropionic acid* ($n=2$).—The crystallographic data given by Groth * for β-phenylpropionic acid are as follows, the measurements being due to Fock † and Boris ‡:—Monoclinic prismatic—$a:b:c=1{\cdot}6054:1:0{\cdot}05552$, $\beta=101°\ 13'$, $d=1{\cdot}142$. The forms observed are {100}, {010}, {120}, {110}, {320}, and occasionally {001} and {111}. There is no apparent cleavage, and one of the optic axes is perpendicular to the (100) face.

Rotation photographs taken about the three crystallographic axes given by Groth gave the following values for the primitive translations along them :—

$$a=32{\cdot}2\ \text{Å.},\quad b=9{\cdot}83\ \text{Å.},\quad c=5{\cdot}54\ \text{Å.}$$

This corresponds to an axial ratio $a:b:c=3{\cdot}28:1:0{\cdot}563$, from which it is seen that the value of the true "a" translation is twice that obtained from goniometrical measurements. All indices except those given above will refer to the new cell with doubled "a" axis. The crystallographic "β" angle was confirmed within the error-limit by a Laue photograph. The volume of this cell is $V=1720$ Å.^{3}, the molecular weight ($C_9H_{10}O_2$) is $M=150$, and the density $d=1{\cdot}142$. The number of molecules in the unit cell is then given by $n=V\,.\,d/M\,.\,m_H$, where m_H is the mass of the hydrogen atom. A substitution of the above values gives $n=7{\cdot}94$ (8) molecules per unit cell.

The theoretical rotation diagrams from these measurements have been given by Bernal § as an example of the use of his methods in the interpretation of rotation photographs. It is readily seen by reference to his figures that the rotation about the "c" axis is useless except for the determination of the translation, the relations of the spots to one another being such that it is impossible to resolve them. In the photographs taken about the "a" and "b" axes and the normal to the (100) face the planes given in Table II. were identified.

* v. Groth, *Chemische Kristallographie*, iv. p. 578.

† Fock, *Zeits. für Krist.* xix. p. 463 (1891).

‡ Boris, *Atti d. Soc. Ital. d. Sc. Nat. Milano*, xli. p. 46 (1902).

§ Bernal, *loc. cit.* figs. 13–17. N.B.—The dimensions given by him apply to a reciprocal lattice constructed for CuK_α radiation ($\lambda=1{\cdot}54$ Å.). The value for the translation along the "a" axis has since been slightly altered in the light of more recent measurements. The translations of the reciprocal lattice referred to FeK_α ($\lambda=1{\cdot}93$ Å.) used in the present paper are $a^*=0{\cdot}060$, $b^*=0{\cdot}196$, $c^*=0{\cdot}356$.

Table II.

$C_6H_5CH_2CH_2COOH$.

"a" axis.			"a" face normal.	"b" axis.
200	620	002	110	200
400	820	112	310	400
600	920	$\bar{7}12$	510	110
110	430	$\bar{8}12$	710	210
210	111	122	910	310
310	311	$\bar{1}22$	430	510
510	411	$\bar{2}22$		$11\bar{1}$
610	811	$\bar{3}22$		220
710	021			320
910	121			420
				430

Miss K. Yardley has very kindly made measurements of the relative intensities of reflexion from the [001] and the [010] zones, using the Bragg spectrometer. The heights of the reflexion peaks in terms of an arbitrary scale are given uncorrected except for general scattering in Tables III. and IV. A further correction of these measurements is at present unprofitable.

Table III.

$C_6H_5CH_2CH_2COOH$.

Spectrometer Measurements: Planes $\{hk0\}$.

2,00	85	1,10	23	0,20	16	1,30	2	0,40	2·5
4,00	11	2,10	7	1,20	5	2,30	1·5	1,40	3·0
6,00	57	3,10	22	2,20	40·5	3,30	3	3,40	8·0
8,00	1·5	5,10	11	3,20	17	4,30	7	6,40	1·5
10,00	2·5	6,10	5	4,20	91	6,30	3·5	8,40	3·5
12,00	18	7,10	22	6,20	16	7,30	1	.....	
14,00	11	8,10	1·5	8,20	7·5	8,30	2	5,50	1·5
16,00	7	9,10	3·5	9,20	4·8	9,30	1·5		
18,00	7·5	11,10	6	10,20	4				
20,00	0·7	13,10	8	12,20	3				
22,00	0·8	14,10	2·5	14,20	3				
24,00	0·2	15,10	1						

The following reflexions were looked for, but not found:—($h00$) when h odd, also (26,00) (28,00) (30,00); ($0k0$) when k odd, also (060); (410) (10,10) (12,10); (520) (720) (13,20); (530) (12,30) (15,30); (240) (440) (540) (740) (10,40) (12,40); (150) (10,50); (260) (360) (660) (860) (10,60) (12,60); (980).

TABLE IV.

$C_6H_5CH_2CH_2COOH$.

Spectrometer Measurements: Planes {*hol*}.					
001	17	60$\bar{1}$	34	6 02	4
20$\bar{1}$	28	600	57	12,01	5·5
20$\bar{2}$	15·5	601	7	12,01	4·5

No planes of the form (*hol*) when *h* was odd were found. Further, reflexions from the following planes were looked for, but not found :—(002) (003) (004); (201) (202) (203) (204); (401) (402) (403) (404) (604); (20$\bar{4}$) (20$\bar{6}$); (40$\bar{1}$) (40$\bar{2}$) (40$\bar{3}$) (40$\bar{4}$); (60$\bar{2}$) (60$\bar{3}$) (60$\bar{4}$); (80$\bar{1}$) (80$\bar{2}$); (10,0$\bar{1}$) (10,0$\bar{2}$); (12,0$\bar{2}$); (14,0$\bar{2}$). The values of the intensities given in this table have been multiplied by a factor 1·54 to reduce the measurements in the two zones to the same arbitrary scale.

An examination of Tables II.–IV. shows that planes are present of all types of the general form {*hkl*} and of the form {*hol*} when $(h+l)$ is odd and when *l* is odd, but no plane of the form {*hol*} when *h* is odd. Further, no trace could be found of the odd orders of the plane (010) by oscillation or by the spectrometer measurements. The only space-group of the prismatic class of the monoclinic system (or, for that matter, of the system as a whole) which satisfies these conditions is $C_{2h}^5(a)$ *.

The elementary cell here given shows no agreement with that given by Becker and Jancke †. Their measurements were, however, entirely based on the interpretation of powder photographs at a time when its untrustworthiness for crystals of low symmetry was not fully recognized.

(iii.) *γ-phenylbutyric acid* ($n=3$).—This substance is very similar to phenylacetic acid in its properties. It crystallizes in rhombic flakes {100} with an angle 51° 30′. The flakiness is, if possible, more pronounced than in phenylacetic acid, as single crystals could only be obtained by their quick removal from a partially solidified melt of the substance. The optical properties are entirely similar to those of phenylacetic acid as observed qualitatively under the polarizing microscope. The boundary faces of the flakes were again of the zones [011] and [01$\bar{1}$].

The elementary cell which was found to agree with the observations was

$$a=17{\cdot}8\ \text{Å.},\quad b=4{\cdot}90\ \text{Å.},\quad c=10{\cdot}3\ \text{Å.},\quad \beta=98°\,30'.$$

* Astbury & Yardley, *loc. cit.*

† Becker & Jancke, *loc. cit.*

The method of analysis followed was similar to that of phenylacetic acid. The indices of the planes identified are given in Table V.

Table V.

$C_6H_5CH_2CH_2CH_2COOH$.

"b" axis.		"c" axis.	"a" face normal.
100	011	300	110
300	210	110	111
$20\bar{2}$	$11\bar{1}$	210	$21\bar{1}$
110	$21\bar{1}$	111	$31\bar{1}$
		$31\bar{1}$	

No trace was found of the (010) or of planes of the type (*hol*) when l was odd. The absence of this latter type of plane was particularly to be noticed in the rotation about the normal to the "a" face, where all this class falls together in vertical lines, and in the "c" axis photograph, where the first-layer line is only very sparsely occupied. The space-group which satisfies these conditions is $C_{2h}^5(b)$ *, with four molecules in the elementary cell.

(iv.) *δ-phenylvaleric acid* ($n=4$).—Only a purely preliminary survey of this acid has been made. Rotation photographs about the "b" and "c" axes and about the normal to the (100) face have been taken. The following measurements can be given :—

$$b=7\cdot13, \qquad c=11\cdot32, \qquad d_{100}=8\cdot73.$$

The crystal class is monoclinic. The investigation was not carried further, as a complete change in the crystal structure has taken place, and a deeper discussion was deemed unprofitable. The number of molecules which would be required in an elementary cell of these dimensions would be four.

(v.) *Summary.*—In Table VI. the measurements are summarized. Those of Sir William Bragg † on benzoic acid are introduced to make comparison easier.

* Astbury & Yardley, *loc. cit.*
† *Loc. cit.*

TABLE VI.

$C_6H_5[CH_2]_nCOOH$.

	W. H. Bragg.	Present investigation.			
n	0	1	2	3	4
a	21·6	14·2	31·6	17·8	—
b	5·18	4·90	9·83	4·90	7·13
c	5·44	10·1	5·54	10·3	11·32
β	97° 05′	101°	101° 30′	98° 30′	—
d_{100}	21·5	13·9	15·4	17·7	8·73
Mols. per cell	4	4	8	4	4 (?)
Space-group	$C_{2h}^5(a)$	$C_{2h}^5(b)$	$C_{2h}^5(a)$	$C_{2h}^5(b)$	—
$d_{cal.}$	1·34	1·30	1·17	1·22	1·01 (?)
$d_{obs.}$	1·29	1·23	1·14	—	—
Mol. wt.	122	136	150	164	178
Melting-pt.	121°	77°·5	48°·7	42°	58°–59°

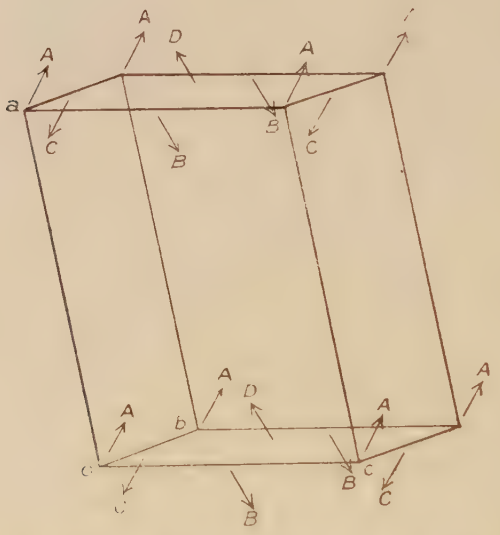
3. DISCUSSION.

From a survey of the dimensions of the unit cells of the substances investigated in comparison with that of benzoic acid, it is seen that a very radical change has taken place. It is reasonable to suppose that this alteration is due to a change in the linkage between the molecules in the crystal. From the point of view of the chemist, benzoic acid is purely an aromatic acid; while from ε-phenylcaproic acid ($n=5$) onwards * the side-chain seems to predominate, and the substances tend in their properties to the aliphatic acids. The substances which have been investigated represent the stage in the series where the properties go over from the aromatic to the aliphatic. The change in the crystal structure is apparently linked up with the change in the chemical properties. The variation is not a continuous one, as might be expected, but something much more complicated. Each CH_2 group which is added seems to alter the linkage between the atoms to a very considerable degree. The similarity between phenylacetic acid and γ-phenylbutyric acid suggests that the series finally settles down to a double series of alternating odd and even numbered acids similar to the fatty acids themselves. The relations between these two acids are very close. The lengths of the "b" and "c" axes are the same within the limits of experimental error. The

* Borsche, *Ber.* 1919, p. 2084; Braun, *Ber.* 1911, p. 2873.

arrangements of the molecules corresponding to the modification of the space-group C_{2h}^5 met with in this case is shown in fig. 1. The molecules B are derived from A by a translation $c/2$ and a reflexion in the symmetry plane. The molecules C and D are derived from A and B by the operation of a set of diagonal screw-axes parallel to the "*b*" axis at a distance $c/2$ apart. This arrangement, and the dimensions of the cell, would be consistent with an arrangement of the molecules with their carboxyl groups

Fig. 1.



together *. There is an increase in the length of the "*a*" axis of 3·8 Å., roughly that required by the addition of four CH_2 groups. This suggests that the greatest length of the molecule lies in the general direction of the "*a*" axis. A discussion of the intensities of reflexions is at present useless owing to the extreme thinness of the flakes in which these acids crystallize.

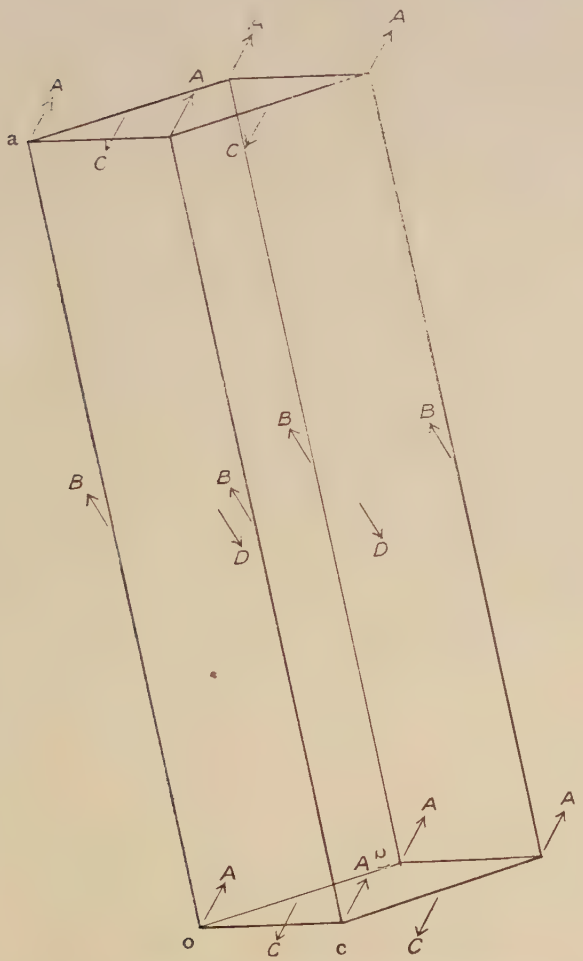
In the case of the even-numbered acids no simple relation exists, except the recurrence of a value of 5·5 Å. in the "*c*" axis of benzoic and β-phenylpropionic acids, and twice that in δphenylvaleric acid.

The space-group of β-phenylpropionic acid is given in fig. 2. In reality it is the same as that of fig. 1, with an

* Shearer, Proc. Roy. Soc. A, cviii. p. 655 (1925).

interchange of "*a*" and "*c*" axes. In this case each asymmetric group consists of two molecules. In the case of benzoic, which is of the same space-group, each asymmetric group consists of only one molecule. It is not

Fig. 2.



profitable to discuss the structure of these acids further, owing to the very large number of variables which may enter into the most simplified conception of the molecules.

It is perhaps interesting to call attention to the fact that

the sudden alteration in the crystal habit of δ-phenylvaleric acid is suggested by the anomalous melting-point. The next members of the series are oils at ordinary temperatures *.

In conclusion, the author wishes to express his very great indebtedness to Prof. Sir William Bragg, who suggested this work, for his continued interest and encouragement, and to the Workers of the Davy-Faraday Laboratory—especially Miss Yardley, Mr. Saville, and Mr. Bernal—for their invaluable assistance and discussion. He is also indebted to the Managers of the Royal Institution for the provision of laboratory accommodation, and to the Dean and Faculty of Arts of McGill University, Montreal, Canada, for the award of a Moyse Travelling Fellowship during the tenure of which this work was carried out.

The Davy-Faraday Laboratory,
Royal Institution, London, W. 1.
April 8, 1927.

CXXI. *On the Voltage necessary to maintain a Luminous Discharge in Hydrogen.* *By* W. Albert Noyes, jr., *D.-es-Sc., University of Chicago*†.

IN an article published in 1922, Gibson and Noyes reported some experiments on the voltage necessary to maintain the luminous discharge in hydrogen and in mercury vapour ‡. It was shown that the voltage necessary to maintain the luminous discharge was intimately related to the ionization potentials of the gases in question. Since that time McCurdy has published articles on the same subject §. Since there are some points of disagreement between the two researches, it may be well to point out wherein the differences are real, and to attempt an explanation of the points of divergence.

The two researches seem to be in agreement upon the following points:—(1) The distance between striations in the striated discharge may be expressed as a function of the dimensions of the tube in the case of hydrogen by the formula of Wehner ‖. (2) There seem to be two types of discharge which McCurdy has designated as A and B.

* Borsche; also Braun, *loc. cit.*
† Communicated by the author.
‡ Journ. Am. Chem. Soc. xliv. p. 2091 (1922).
§ Phil. Mag. xlvi. p. 524 (1923).
‖ *Ann. der Physik*, xxxii. p. 49 (1910).

(3) The characteristics of the discharge and the voltage of disappearance are functions of the current through the filament, but approach constancy for high filament currents. (4) The voltage necessary to start the glow is always higher than the voltage at which the glow disappears as the potential difference between the electrodes is gradually diminished. (5) At very low pressures the voltage at which the glow disappears is not very reproducible, but is higher than the disappearance voltage at somewhat higher pressures. (6) As regards the work on mercury vapour, the agreement seems to be excellent, as it was pointed out in both papers that the discharge usually disappears at a voltage which is some multiple of the ionization potential, or some multiple of the ionization potential plus the first resonance potential.

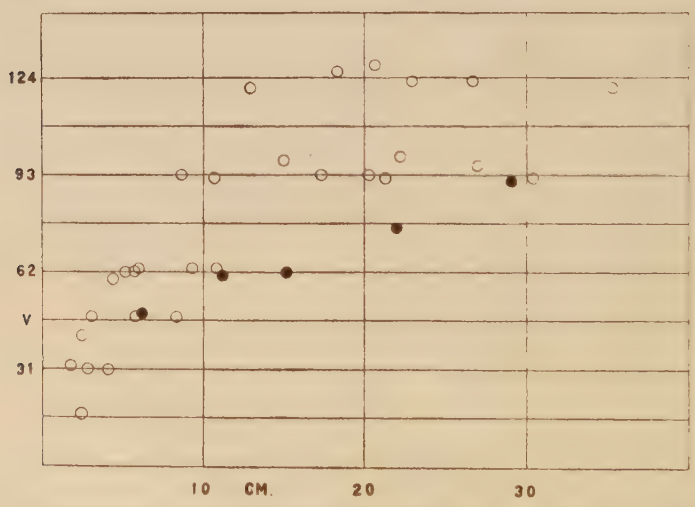
There is, however, one point of disagreement. In the case of hydrogen, Gibson and Noyes found that the pressure-disappearance voltage curve passes through a minimum for a given tube, and that this minimum was, in many cases, some multiple of 31 volts. Inspection of their published data reveals the fact that this was not always the case. McCurdy apparently found lower voltages of disappearance, and while, in the case of the striated discharge, his curves of minimum disappearance voltage against length of tube flatten out at definite points, these points are not multiples of 31 volts, but are (to judge from his curve) about multiples of twenty volts. For the non-striated discharge he found a smooth curve when the minimum disappearance voltage was plotted against the length of tube, although this curve passes through a minimum at a tube-length of about three centimetres and a voltage of 31 volts.

Inspection of the descriptions of the experimental procedures used reveals the fact that they were very similar. There is only one difference which might possibly be important. McCurdy used a spiral tungsten filament, whereas Gibson and Noyes used a straight-wire tungsten filament. It is difficult to decide whether this is really an important difference, although one or two experiments did indicate some differences in behaviour of the discharge when the two filaments were used. The differences were in the direction which might be expected from the discrepancy in the data presented.

It is not desired to advocate this method as a method of measuring ionization potentials, nor is it desired to insist upon the theoretical presentation in the previous article. The excellent work carried out in the Princeton Laboratory

has gone far toward a complete explanation of the phenomena observed in discharge-tubes.

Some experiments similar to those performed by Gibson and Noyes have recently been carried out. An attempt was made to reduce the personal factor in the observations to as great an extent as possible by the use of a system of resistances in connexion with the voltmeter in such a manner that it was necessary to calculate the disappearance voltages after the run. Phenomena somewhat similar to those previously reported have been observed. When a tube is first used, the voltage of disappearance of the glow is not reproducible, due perhaps to the presence of air and of water vapour. It was found that the results became reproducible after continued operation. The diagram shows the variation of minimum disappearance voltage with length of tube. Tubes of many different diameters are shown in the same diagram. Circles represent points obtained by Gibson and Noyes, while the solid points were recently obtained. The horizontal lines are arbitrarily drawn at intervals of 15·5 volts.



Inspection of the diagram reveals the fact that most of the points obtained are in the vicinity of the lines which represent the multiples of 15·5 volts. It would seem that the value of 31 volts may be without especial significance, except in so far as it is twice 15·5. 15·5 volts is not far from the accepted ionization potential of hydrogen. Undoubtedly the phenomena in hydrogen are complicated by the fact that the gas is diatomic; but it would seem that

under certain conditions, at least, that the discharge may disappear at some voltage which is approximately a multiple of the ionization potential. As Professor Compton has pointed out, the possibility of small variable potential drops in the neighbourhood of the electrodes would make it seem likely that the relation pointed out cannot be universal or exact. Inspection of the diagram will show that some points differ by more than the experimental error from some multiple of the ionization potential.

In conclusion, it would seem that the differences between the two researches are more apparent than real, and that they are in excellent agreement in most respects.

CXXII. *On the detailed Explanation of Spectra of the Metals of the Second Group. By* MEGHNAD SAHA, *Professor of Physics, University of Allahabad, India* *.

THE explanation of the spectra of elements is now making very rapid strides, thanks to the work on the arrangement of electrons inside the atom on the one hand, and development of the principles of non-mechanical vector addition of quantum numbers on the other hand, which we owe to Landé, Russell, Pauli, Heisenberg, Hund †, and others. The latter authors have so far confined their attention to the fundamental levels of the atom, though in some papers the higher levels have been accounted for on similar lines. In the present paper, an attempt has been made to show that these principles can be extended for finding out all the higher terms, and in the case of metals of the second group all details of their spectra are explained in a very satisfactory way. The following is a brief sketch of the method of working :—In accordance with Pauli's Principle, we assign to each electron the characteristics of a doublet spectrum. Applied to alkalies, the explanation of the spectrum is very easy. The vibrating electron always comes after a sublevel has been completely closed, hence the atomic residue contributes nothing towards the resultant spectrum. The electron may be supposed to run through all the higher levels, beginning from X_1. We thus get ^2S, ^2P, ^2D, ... terms,—*i. e.* a completely developed doublet spectrum. The higher terms arise when the electrons run through the possible higher levels. In the case of alkaline earths, there are two

* Communicated by the Author.

† For a complete bibliography, see a paper by Otto Laporte, Journ. Opt. Soc. Amer., July 1926.

outermost electrons. In the normal case, both are in some X_1-level. But when the atom is excited, one may be supposed to be at rest; the other runs through all the higher levels. The spectrum observed is due to the combination of the orbits of these two electrons. The rules for combination of orbits were first given by Pauli and developed by Hund and Heisenberg. For the sake of lucidity, I have attached a complete structure diagram. The rules of addition of quantum numbers are also summarized below. It may be added that I claim no originality in this paper except the method of representation, which I have found to be very convenient.

Principles of Orbit Combination.

The principles which have so far been developed may be thus briefly summarized :—

Each spectral term may be denoted by the symbol n^r_{kj} (Landé), where r denotes the multiplicity $r=(1, 2, 3, \ldots$ for singlets, doublets, triplets, etc.), $k=$azimuthal quantum number $(1, 2, 3, \ldots$ for $s, p, d, f, \ldots)$, $j=$inner quantum number which is the vector sum of r and k. But for purposes of addition, we do not use r, k as they occur above, but have to use certain associated numbers. Different authors use different symbols with different values : thus Landé uses R, K, J ; Sommerfeld uses j_s, j_a, j ; and Pauli uses $[i, j, k]$. A comparison between the different systems of symbols is given in a recent paper by Otto Laporte, who finds that the Sommerfeld system is superior to the other two. In the following we adopt the Sommerfeld systems with a slight change. We shall write

i_r, in place of Sommerfeld's j_s,

i_k, in place of Sommerfeld's j_k,

i_j, to denote the effective inner quantum number.

Thus

$i_r=0, \frac{1}{2}, \frac{2}{2}, \frac{3}{2}$ for singlets, doublets, triplets, etc.

$i_r=k-1, \quad 0, 1, 2, 3$ for $s, p, d, f, \ldots$.

i_j is calculated from the rule :—

$i_j=$ Vector sum of i_k and i_r in the quantum sense—

i. e. it must have all successive whole or half-numbered values lying between $|i_r+i_k|$ and $|i_r-i_k|$.

For purposes of description, Landé's notation n^r_{kj} may be retained.

Table I. contains a full chart of (i_r, i_j, i_k) values for different systems.

TABLE I.—Showing values of i_r, i_k, i_j.

ODD MULTIPLETS.							EVEN MULTIPLETS.						
i_k \ i_j	0	1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	i_j \ i_k
$s=0$	0				Singlet $i_r=0$		$\frac{1}{2}$				Doublet $i_r=\frac{1}{2}$		$s=0$
$p=1$		1					$\frac{1}{2}$	$\frac{3}{2}$					$p=1$
$d=2$			2					$\frac{3}{2}$	$\frac{5}{2}$				$d=2$
$f=3$				3					$\frac{5}{2}$	$\frac{7}{2}$			$f=3$
$s=0$		1			Triplet $i_r=\frac{2}{2}$			$\frac{3}{2}$			Quartet $i_r=\frac{3}{2}$		$s=0$
$p=1$	0	1	2				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$				$p=1$
$d=2$		1	2	3			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			$d=2$
$f=3$			2	3	4			$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$		$f=3$
$s=0$			2		Quintet $i_r=\frac{4}{2}$				$\frac{5}{2}$		Sextet $i_r=\frac{5}{2}$		$s=0$
$p=1$		1	2	3				$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			$p=1$
$d=2$	0	1	2	3	4		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$		$d=2$
$f=3$		1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$f=3$

The corresponding magnetic quantum number $i_m = \pm i_j$ $\pm i_j - 1$, $\pm i_j - 2$, and thus i_m is the vector sum of i_{mr} and i_{mk}, where

$$i_{mr} = \pm i_r, \quad \pm i_r - 1,$$
$$i_{mk} = \pm i_k, \quad \pm i_k - 1.$$

The change in energy level in weak fields is given by

$$\frac{\mathrm{E}}{\mathrm{O}h} = (i_{mr} + i_{mk})\, g,$$

where

g = Landé's splitting-up factor,

O = Larmor's precession factor $= \dfrac{e\mathrm{H}}{4\pi cm}$.

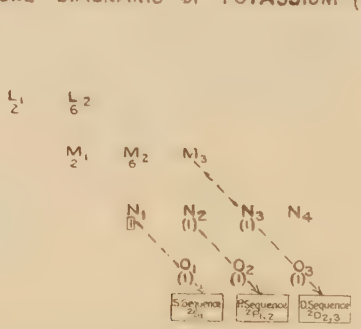
The change in strong fields is given by

$$\frac{\mathrm{E}}{\mathrm{O}h} = 2i_{mr} + i_{mk}.$$

We shall have no occasion to use the strong field or weak field magnetic quantum numbers *.

The doublet spectrum is supposed to be the fundamental spectrum from which all other complicated spectra can be synthesized. When the constitution is such that there is only one electron left after a sublevel is closed, this electron as it runs through the following levels gives rise to the corresponding doublet terms. Thus we have for Potassium :

STRUCTURE DIAGRAMS OF POTASSIUM (19)



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF K.

Russell and Saunders' symbol has been used throughout (*vide* Ap. Journ. vol. lxi. p. 38). (1) denotes the running electron.

* The preliminary introduction is taken from Laporte's article in the Journ. Opt. Soc. America, July 1926.

Thus the alkali spectrum is most simply explained on the assumption that it is due to the movement of the running electron in the successive higher levels.

[Rules of Synthesis.]

Alkaline Earths.

In the case of the next group of elements, viz. the alkalies, a second electron is added. If we take Mg, we have the constitution :—

$$\mathrm{Mg} = \begin{pmatrix} \mathrm{K} & \mathrm{L} & \mathrm{M}_1 & \mathrm{M}_2\ldots \\ 2 & 8 & 1,(1)\rightarrow(1) & \end{pmatrix}$$

The optical spectrum is due to the two outer electrons shown under M_1. In most cases, one electron remains fixed at M_1, the other runs through the successive levels. The level observed is the vector sum of the levels of these two electrons. As mentioned above, these rules have been developed by Russell, Pauli, Heisenberg, and Hund. Let $\mathrm{N}^{\mathrm{R}}_{\mathrm{KJ}}$ denote the resultant levels, and let I stand for the Sommerfeld quantum numbers. Then to get a complete knowledge of $\mathrm{N}^{\mathrm{R}}_{\mathrm{KJ}}$, we must have a knowledge of the corresponding values of I_{K}, I_{J}, I_{R}. We have

$$\mathrm{I}_{\mathrm{R}} = \text{vector sum of } (i_r)_1 \text{ and } (i_r)_2 ;$$
$$\mathrm{I}_{\mathrm{K}} = \text{vector sum of } (i_k)_1 \text{ and } (i_k)_2.$$

The determination of I_{J} presents the most formidable difficulties. It cannot be defined as the vector sum of $(i_j)_1$ and $(i_j)_2$. We have to write out all the possible magnetic levels for each of the components (1) and (2) and then add them, taking one from each group. Thus :—

The magnetic levels of electron (1) are

$$(i_m)_1 = \pm(i_j)_1,\ \pm(i_j)_1-1,\ \pm(i_j)_1-2,\ \ldots,$$

The magnetic levels of electron (2) are

$$(i_m)_2 = \pm(i_j)_2,\ \pm(i_j)_2-1,\ \pm(i_j)_2-2\ \ldots.$$

Thus the above procedure, without any further restriction, would give us

$$\{2(i_j)_1+1\}\{2(i_j)_2+1\} \text{ values of } \mathrm{I}_m.$$

After arranging these values symmetrically, we have to obtain the values of I_j. This will completely define the resultant term I_j.

Applying this rule to Mg, when we have both electrons in the M_1 orbit,

	i_r.	i_k.	i_j.	i_m.	
for electron (1) :	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
„ „ (2) :	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

Resultant : $0 \quad \frac{2}{2} \quad 0 \qquad 0'$

$1 \quad 0 \quad \bar{1}$

$I_R \qquad I_K \qquad I_J = 0, \; I_J = 1$

The resultant orbit has therefore $I_R = 0$ and $\frac{2}{2}$, *i. e.* it belongs to a singlet or triplet system. $I_K = 0$, *i. e.* $K = 1$. It is an *s*-orbit $I_J = 0, 1$. It has the inner quantum number $= 0$ or 1.

Since $^3S_1$ is not observed, Pauli lays down a principle which excludes it, viz. : no two electrons in a closed orbit can have identical values of i_m.

This rule excludes $^3S_1$, for it arises from $(i_m)_1 = \frac{1}{2}$, $(i_m)_2 = \frac{1}{2}$, or both $= -\frac{1}{2}$.

From this principle also follows Stoner's rule : The number of electrons in a closed group $= 2j$ [j used in Landé's sense]. For the resultant magnetic moment due to the component electrons $= 0$, and this can take place if we assign to each the different possible value of $(i)_m$ for a subgroup. The number $= 2j$ or $(2i_j + 1)$, and to every positive value there is a corresponding negative value. Hence the resultant $= 0$, when there are $2j$ electrons, and each is contained in a different magnetic level. But I do not think that Stoner's subdivision of each higher level L_2 or M_2 into $L_{21}\, L_{22}\, M_{21}\, M_{22}$ is quite justified. See a paper by Saha and Ray in the *Physikalische Zeitschrift*.

Origin of Higher Terms.

But Pauli's principle cannot be applied where the electrons are in different levels. Thus let electron (1) be in the M_1-orbit, electron (2) in the N_1-orbit. Here Pauli's rule will not hold ; we shall get $2\,^1S_0$, $2\,^3S_1$-terms. Similarly, as the electron (2) runs through the higher X_{11} levels it gives rise to the higher members of the $^1S_0$ and $^3S_1$ series, viz. $2\,^1S_0$, $2\,^3S_1$, etc.

Combination of M_1 and M_2 Levels.

We have

	i_r.	i_k.	i_j.	i_m.
for electron (1):	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$ $-\frac{1}{2}$
„ „ (2):	$\frac{1}{2}$	1	$(\frac{1}{2}, \frac{3}{2})$	$(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{3}{2})$ $(\frac{1}{2}, \frac{1}{2})$

$$\begin{array}{ccccc} 0 & \frac{2}{2} & 1 & & 0 \quad\quad I_j = 0 \\ \diagdown & \diagup & | & & 1\ 0\ \bar{1} \quad\quad I_j = 1 \\ I_r & & I_k & & 2\ 1\ 0\ 1\ \bar{2} \quad\quad I_j = 2 \\ & & & & 1\ 0\ \bar{1} \quad\quad I_j = 1 \end{array}$$

The resultant orbit will be $^1P_1$, $^3P_{0,1,2}$. The number of magnetic levels for these terms is $3+(1+3+5)=12$. The possible numbers of combinations of $(i_m)_1$ and $(i_m)_2$ are 2 and 6, and if we write them out, and add for the resultant I_m, and write out the corresponding values of J, we get the P terms $(^2S_{\frac{1}{2}}, {}^2P_{\frac{1}{2}})$ give us $^1P_1$, $^3P_0$, and $(^2S_{\frac{1}{2}}, {}^2P_{\frac{3}{2}})$ give us $^3P_1$, $^3P_2$.

Combination of N_1 and N_3 Levels *.

We need not repeat the summation for i_r. Now $I_k=2$, or the resultant are D-terms, $^1D_2$, $^3D_{1,2,3}$. The values of i_j are $\frac{1}{2}$ and $(\frac{5}{2}, \frac{3}{2})$ respectively. $(\frac{1}{2})$, $(\frac{3}{2})$ give us $^1D_2$, $^3D_1$, and $(\frac{1}{2})$, $(\frac{5}{2})$ give us $^3D_{2,3}$. In this way we get by combination with levels N_2 the higher Rydberg terms of $^1P_1$ and $^3P_{0,1,2}$. Combination with N_4 gives us the first F-terms.

We thus get a general explanation of the regular term-sequences in the spectrum of Mg, and *mutatis mutandis* for Ca, Sr, and Ba as well. But the procedure is capable of yielding still further results. It is known to spectroscopists that, in spite of the similarity amongst the spectra of these elements, there are certain outstanding differences. For the spectrum of Mg, the highest value for the sequence D = 15268·7, while the highest D-values for Ca, Sr, and

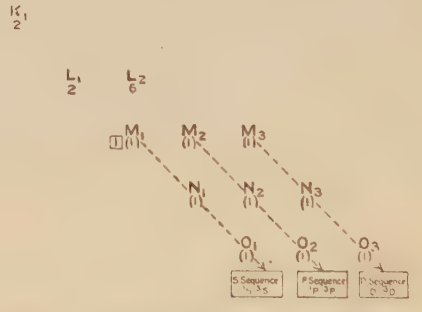
* Fowler, Report on Series in Line Spectra, ch. xiv.

Ba are much higher ; in fact they sometimes exceed the P-values, as the following table shows :—

	D.		P.	
Mg	$^1D_2$	15268·7	$^1P_1$	26620·7
	$^3D_2$	13714·7	$^3P_1$	39801·4
Ca	$^1D_2$	27455·3	$^1P_1$	25652·4
	$^3D_2$	28955·2	$^3P_1$	34094·6
Sr	$^1D_2$	25786·8	$^1P_1$	24238·1
	$^3D_2$	27717·7	$^3P_1$	31432·2
Ba	$^1D_2$	30634·1	$^1P_1$	23969·2
	$^3D_2$	32814·1	$^3P_1$	29392·8

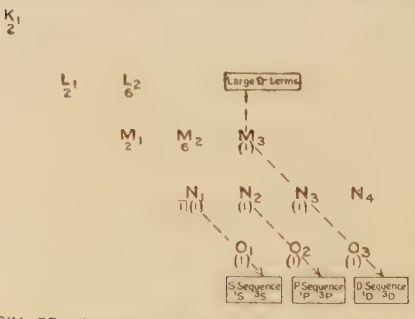
These large D-values can be easily explained if we compare the Structure Diagrams of Mg and Ca.

STRUCTURE DIAGRAMS Mg (12)



ORIGIN OF NORMAL TERMS IN MAGNESIUM

STRUCTURE DIAGRAMS OF CALCIUM (20).



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF CA

A comparison of the two structure diagrams shows that the successive positions of the running electron in Mg are

Chart illustrating Periodic Cla

			K_{2}^{1}	
1	H			
2	HE	$2K_1$		
3	LI	$2K_1$ L_1		L_{2}^{1}
4	BE	$2L_1$		
5	B	$2L_1$ L_2		
6	C	$2L_2$		
7	N	$3L_2$		
8	O	$4L_2$		
9	F	$5L_2$		
10	NE	$6L_2$		
11	NA	$6L_2$ M_1		
12	MG	$6L_2$ $2M_1$		
13	AL	$2M_1$ M_2		
14	SI	$2M_2$		
15	P	$3M_2$		
16	S	$4M_2$		
17	CL	$5M_2$		
18	A	$6M_2$		
29	CU	$10M_3$ N_1 $9M_3$ $2N_1$	19 K	$6M_2$ N_1
30	ZN	$10M_3$ $2N_1$	20 CA	$6M_2$ $2N_1$
31	GA	$2N_1$ N_2		
32	GE	$2N_1$ $2N_2$		
33	AS	$3N_2$		
34	SE	$4N_2$		
35	BR	$5N_2$		
36	KR	$6N_2$		
47	AG	$10N_3$ O_1	37 RB	$6N_2$ O_1
48	CD	$2O_1$		
49	IN	$2O_1$ O_2	38 SR	$6N_2$ $2O_1$
50	SN	$2O_2$		
51	SB	$3O_2$		
52	TE	$4O_2$		
53	I	$5O_2$		
54	XE	$6O_2$		
79	AU		55 CS	$6O_2$ P_1
80	HG	$10O_3$ $2P_1$	56 BA	$6O_2$ $2P_1$
81	TL	$2P_1$ P_2		
82	PB	$2P_2$		
83	BI	$3P_2$		
84	PO	$4P_2$		
85	RAD Te	$5P_2$		
86	NT	$6P_2$		
			87 EKA CS	$6P_2$ Q_1
			88 RA	$6P_2$ $2Q_1$

[*To face* p. 1273.

Electronic Composition of Atoms.

Transitional Group I.	Transitional Group II.	Rare Earths I.	Transitional Group III.
21 Sc $M_3\ 2N_1$ / $2M_3\ N_1$	39 Y $2N_3\ O_1$ / $N_3\ 2O_1$	57 La	71 Lu
22 Ti $2M_3\ 2N_1$ / $3M_3\ N_1$	40 Zr $3N_3\ O_1$ / $2N_3\ 2O_1$	58 Ce	72 Hf $2O_3\ 2P_1$ / $3O_3\ P_1$
23 V $3M_3\ 2N_1$ / $4M_3\ N_1$	41 Cb $4N_3\ O_1$ / $3N_3\ 2O_1$	59 Pr	73 Ta $3O_3\ 2P_1$ / $4O_3\ P_1$
24 Cr $5M_3\ N_1$ / $4M_3\ 2N_1$	42 Mo $5N_3\ O_1$ / $4N_3\ 2O_1$	60 Nd	74 W $4O_3\ 2P_1$ / $5O_3\ P_1$
25 Mn $5M_3\ 2N_1$ / $6M_3\ N_1$	43 Ma $6N_3\ O_1$ / $5N_3\ 2O_1$	61	75 Re $5O_3\ 2P_1$ / $6O_3\ P_1$
26 Fe $6M_3\ 2N_1$ / $7M_3\ N_1$	44 Ru $7N_3\ O_1$ / $6N_3\ 2O_1$	62 Sm	76 Os $6O_3\ 2P_1$ / $7O_3\ P_1$
27 Co $7M_3\ 2N_1$ / $8M_3\ N_1$	45 Rh $8M_3\ O_1$ / $7M_3\ 2O_1$	63 Eu	77 Ir $7O_3\ 2P_1$ / $8O_3\ P_1$
28 Ni $8M_3\ N_1$ / $9M_3\ M_1$	46 Pd $10N_3$ / $9N_3\ O_1$	64 Gd	78 Pt $9O_3\ 2P_1$ / $9O_3\ P_1$
		65 Tb	
		66 Dy	
		67 Ho	
		68 Er	
		69 Tm	
		70 Yb	

M_{6}^{2} M_{10}^{3}

N_{2}^{1} N_{6}^{2} N_{10}^{3} N_{14}^{4}

O_{2}^{1} O_{6}^{2} O_{10}^{3}

P_{2}^{1} P_{6}^{2} P_{10}^{3}

Q_{2}^{1} Q_{6}^{2}

M_1 ($^1S_0$), M_2 (^1P and ^3P), M_3 (^1D and ^3D), and we have approximately $^1P = \frac{N}{2^2}$, $^1D = \frac{N}{3^2}$. But in Ca the positions are N_1 ($^1S_0$), N_2 (^1P, ^3P), and then M_3 not N_3, which is on a higher level. Now the ^1D-term corresponding to N_3 has the normal value, *i. e.* Ca $\frac{N}{3^2}$, but the ^1D-term corresponding to M_3 must have a higher value, *i. e.* Ca $\frac{N}{2^2}$. This diagram, therefore, symbolically explains the origin of the large D-terms in Ca and also in Sr and Ba. In the spark spectrum of Ca^+, it explains why the first of ^2D-terms is larger than ^2P, while in the spectrum of Mg^+, ^2P is $> {}^2D$.

[*Explanation of the Chart.*]

[The chart is a modification of the earlier schemes of Bohr and Stoner. The L_{21} and L_{22} levels of Stoner are compounded into one L_2-level. (For explanation, see a paper by Saha and Ray in the *Physikalische Zeitschrift.*) The chart explains the formation of (1) the regular groups, (2) the transitional groups, (3) the rare earths, and gives the electronic composition of the outer shells of the electrons, as obtained from Hund's interpretation of complex spectra (*Zs. f. Phys.* vols. xxxiii. & xxxiv.). The same chart explains the periodic classification, and the spectra of elements. The distinctive nature of the small groups of two, consisting of an alkali and alkaline earth, is clearly brought out. They are formed when any X_1-level ($X = K, L, M, N \ldots$) is filled, just as the regular groups are obtained when X_2 is filled, transitional groups when X_3 is being filled, and rare earths when X_4 ($X = N$) is being filled.

For the explanation of spectra with the same chart, see the text.]

Concluding Remarks.

The foregoing work shows that the above scheme of electron arrangement, which is a modification of Stoner's scheme, combined with the rules of synthesis of complicated spectra from the elementary component doublet spectra, gives a very satisfactory explanation of the fundamental as well as of all the higher terms, regular and anomalous, of the alkaline earths. Even the detailed differences (*e. g.* occurrence of large D-terms in Ca, Ba, Cr, and its absence in Mg) are readily explained. But the theory goes still further. It gives us a clue to the origin of dashed terms.

They arise when the stationary electron is in the metastable orbit, and the running electron is in the same orbit or in the higher homologous orbit. We can also obtain some clue regarding the term values. If the orbit arises when both electrons are in the same shell, or the running electron in the previous unclosed shell, the values are large. No matter whether we get S, P, D, F, or G terms, the order of the value will be the same, when the origin of these terms is common. The origin of dashed terms is taken in a subsequent paper.

Thus note that when both electrons in Ca are in M_3-levels, we get $^3\overline{F}$, $^3\overline{P}$, ^1G, ^1D, $^1S_0$ terms. Their order of value is the same.

But if the running electron is in a higher shell, it will give rise to higher Rydberg terms ; the values will decrease approximately as $\frac{N}{m^2}$, $m=1, 2, 3$ respectively.

The investigation also shows that differences are expected between the spectra of Ca and Ba. These points are being investigated. It is also apparent that for the calculation of the higher Rydberg terms Pauli's rule is not necessary, and we no longer need the complex calculation involving the magnetic quantum numbers.

In conclusion, the author wishes to express his thanks to Mr. K. Mazumder, who has drawn the charts and tables for him.

CXXIII. *On the Variation of the Velocity of Sound in Gases with Temperature.* *By* Eric J. Irons, *B.Sc., Department of Physics, East London College* *.

Abstract.

Formulæ to represent experimental data for the variation of the velocity of sound in gases with the absolute temperature are proposed and discussed.

1. *Introduction.*

So far as the author is aware, no formula proposed up to the present time has been successful in representing with sufficient accuracy over a considerable temperature range the relation between V, the velocity of sound in a gas,

* Communicated by Prof. C. H. Lees, F.R.S.

and T, the absolute temperature, supplied by the researches of Dixon, Campbell, and Parker[1] and of Partington and Shilling[2,3,&3a]. The object of these investigators was to trace the variation with temperature of the ratio γ of the specific heats of certain of the more common gases up to about 1000° C. : the former workers by observing the time taken by a sound-wave to travel through the gas contained in a coiled tube of known length, and the latter by measuring half wave-lengths of stationary waves formed in a straight tube by a source of known frequency.

The accuracy with which their tabular results for the speed of sound can be represented by formulæ of the types:

$$\text{A.} \quad V = a + b\sqrt{T},$$

$$\text{B.} \quad V = bT^n,$$

$$\text{C.} \quad V = a + bT^n,$$

$$\text{D.} \quad V = b(T + a)^n,$$

$$\text{E.} \quad \frac{V}{\sqrt{T}} = b + cT^n$$

(where a, b, c, and n are constants peculiar to the gas considered) is investigated, and the results are discussed in this paper.

2. *Methods of Calculation and Results.*

Type A.—The constants a and b were determined by the methods of least squares.

Type B.—The constants b and n were determined from the form $\log V = \log b + n \log T$ by the method of least squares.

[1] Proc. Roy. Soc. A, c. p. 1 (1921).

[2] For a preliminary account of methods and results for Air, see Trans. Faraday Soc. xviii. part 3, p. 386 (1923); and for later results,

[3] "The Specific Heats of Gases," Partington and Shilling (Ernest Benn Ltd., 1924), p. 141.

[3a] *Additional Note.*—Since the main part of this paper was written, a paper has been published in this journal by W. G. Shilling (Phil. Mag. vol. iii. no. 14, p. 273, 1927), giving an account of the determination of the specific heats of carbon dioxide, nitrous oxide, and steam, by the velocity of sound method.

The results for carbon dioxide are similar to those already given[3]. It is of interest to note that the author states that his figures "uncorrected for the ·5 per cent. of air present are much nearer those of Dixon."

The additional results have been added to the Table of Experimental Data under the initial "S," and the agreement between them and the values calculated from formulæ of Types C and D (see below) are shown in Tables C and D.

Type C.—For determining the constants of this formula one of two methods was employed, either

(*a*) A graphical method described by Running *, or

(*b*) A method of successive approximations as follows :— From four simultaneous values of V and T (V_1, T_1 : V_2, T_2, ...), a and b are eliminated, giving

$$\frac{V_1-V_2}{V_3-V_4}=\frac{T_1^n-T_2^n}{T_3^n-T_4^n},$$

which may be written as

$$\frac{V_1-V_2}{V_3-V_4}=\left(\frac{T_1}{T_3}\right)^n\cdot\left(\frac{1-\left(\frac{T_2}{T_1}\right)^n}{1-\left(\frac{T_4}{T_3}\right)^n}\right).$$

Arranging for T_2/T_1 and T_4/T_3 to be small, it is possible to solve for n by successive approximations, the first of which is to put $n=\cdot5$ in the small terms. The value of b taken is the mean found from such expressions as $V_1-V_2=(bT_1^n-T_2^n)$; while a is the mean value found from $V-bT^n$ for each temperature.

Type D.—The formula may be written as $T=-a+\frac{1}{b^{\frac{1}{n}}}V^{\frac{1}{n}}$ which enables $\frac{1}{n}$ to be determined by Running's method. It was then found better to plot $V^{\frac{1}{n}}$ against T and to find b and a from the resulting straight line rather than to proceed further by Running's method. As it was difficult to determine the reciprocal of n to more than three significant figures, n is given to two only except in the case of steam.

Type E.—Plots of $V/\sqrt{T}$ against T approximated to straight lines for air, nitrogen, and oxygen so that the constants b and c were determined by the method of least squares. The results obtained by Dixon and his collaborators for carbon dioxide and methane formed smooth curves, and the graphical method referred to under Type C was employed to evaluate the constants. The results obtained by Partington and Shilling for carbon dioxide did not yield a smooth curve, and showed a noticeable departure from a straight line, and, in consequence, are omitted.

The results are tabulated under the experimental data ; the first table for each type gives the values of the constants, and the second the value of $V_{observed}-V_{calculated}$ for each temperature.

The velocity of sound is given in metres/sec. throughout the paper.

* Running, 'Empirical Formulas' (Chapman & Hall Ltd., 1917), Second Method, p. 48.

3. *Discussion of Results.*

Type A. $V=a+b\sqrt{T}$. Elementary theory suggests that V is proportional to $\sqrt{T}$: a plot of V against $\sqrt{T}$ did not yield a straight line passing through the origin, but it appeared to be sufficiently rectilinear to justify the calculation of the constants a and b. The results in Table A 2 indicate a distinct curvature, which is confirmed by the variation of b in the two sets of observations for the same gas over the two temperature ranges. The discrepancies in the value of a result from this difference in b.

Type B. $V=bT^n$ has the advantage of simplicity in only possessing two constants, and is in better agreement with experiment, except in the case of methane, although the curvature noted under A still persists. Slightly better agreement may be obtained by calculating n to five decimal places—a procedure hardly justified by the accuracy of the experimental results.

Type C. $V=a+bT^n$. The failure of formula B to eliminate the curvature suggested an alternative of the Type C, where it was found to be less pronounced, if not entirely eliminated. For the same gas the values of the indices n are in better agreement. Methane appears to be anomalous with $n > \cdot 5$ and a positive.

Type D. $V=b(T+a)^n$ with n given to two significant figures shows better agreement than Type B (even for the gases for which a is small): it is not quite as good as Type C.

Type E. $V/\sqrt{T}=b+cT^n$. Table E 2 shows good agreement between calculated and observed values.

It is seen that the values for methane cannot be expressed by the formulæ proposed to the same degree of approximation as those for the other gases. This may be due either to the lack of a suitable formula to express the results, or to changes in the nature of the gas. Dixon and his collaborators (who limit the temperature range of their observations) note that the gas begins to decompose, yielding hydrogen and carbon at a temperature of 700° C. in a silica tube, and it is elsewhere stated * that "when passed through a hot tube a small portion is converted into naphthalene. At higher temperatures it is more or less dissociated in amount dependent on the temperature, and the amount and nature of the heated surface."

* Thorpe's 'Dictionary of Applied Chemistry,' iv. p. 314 (1922).

TABLE OF EXPERIMENTAL DATA.

Temp. Abs.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide.		Methane.	Steam.	Nitrous Oxide.
	D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.	S.	S.
273	331·8	331·4	337·5			258 3		429·2		264·6 *
373	387·5	387·2	394·1	394·1	367·4	300·4	299·9	487·4	471·5	299·0
473	435 8	435·6	443·1	443·3	413·5	336·9	335·85	540·0	536·7	334·3
573	479·0	478·9	487·2	487·4	454·8	369·3	367·51	587·3	593·2	365·4
673	518·6	518·4	527·3	527·5	492·3	398 6	397·11	630·8	643·2	393·9
773	555·2	555·1	564·5	564·7	527·4	425 7	424·0	671·4	688·2	420·3
873	589·3	589 3	599·4	599·4	559·9	450·9	449·2	709·2	727·8	(446·9) †
973	621·6	621·5	632·2	632·3	590·8		472·0		762·5	
1073		651·7	663·0	663·0	619·8		494·5		795·3	
1173		680·5	692·4	692·3	647·8		515·8		825·0	
1273		708·0	720·6	720·6	675·0		536·5		853·9	

* This is the value for 287·5 abs.

† In determining the constants of the formula of Type C for nitrous oxide, this reading was neglected owing to the dissociation of the gas. (See Shilling, Ref. 3 *a*.)

TABLES A 1 & A 2.—Formula $V = a + b\sqrt{T}$.

A 1.	Constants.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide.		Methane.
		D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.
	a.	5·99	7·72	8·03	9·70	5·25	14·70	22·11	71·92
	b.	19·749	19·662	19·997	19·944	18·768	14·788	14·428	21·551
A 2.	Temp. °Abs.								
	273	−·5	−1·2	−·9			−·7		1·2
	373	·1	−·3	−·1	−·8	−·3	·1	−·9	−·7
	473	·3	·3	·2	−·2	·1	·6	·0	−·6
	573	·3	·5	·5	·3	·3	·6	·0	−·5
	673	·3	·6	·5	·4	·2	·3	·7	−·2
	773	·1	·7	·5	·5	·3	·2	·8	·3
	873	−·2	·6	·5	·4	·1	−·7	·8	·5
	973	−·4	·5	·4	·5	·1		−·2	
	1073		−·1	−·1	·0	−·2		−·2	
	1173		−·6	−·5	−·5	−·2		−·5	
	1273		−1·2	−·9	−·7	·1		−·4	

TABLES B 1 & B 2.—Formula $V = bT^n$.

B 1.	Constants.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide		Methane.
		D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.
	b.	20·812	20·899	21·320	21·434	19·620	17·584	18·211	37·061
	n.	·4938	·4930	·4926	·4918	·4949	·4792	·4732	·4334
B 2.	Temp. °Abs.								
	273	−·3	−·6	−·4			−·2		2·1
	373	·0	·0	·0	−·2	−·3	·2	−·2	−1·6
	473	·1	·3	·1	·1	·0	·5	·1	−2·0
	573	·0	·4	·3	·4	·1	·5	−·2	−1·7
	673	·1	·4	·2	·4	−·1	·2	·3	−·7
	773	−·1	·5	·2	·4	·1	·0	·3	·8
	873	−·3	·4	·3	·3	−·1	−·4	·4	2·3
	973	−·5	·3	·2	·4	−·1		−·4	
	1073		−·2	−·2	−·1	−·4		−·3	
	1173		−·7	−·6	−·5	−·4		−·3	
	1273		−1·3	−·9	−·6	·0		·0	

Tables C 1 & C 2.—Formula $V = a + bT^n$.

C 1.	Constants.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide.		Methane.	Steam.	Nitrous Oxide.
		D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.	S.	S.
	a.	−13·8	−14·0	−16·4	−16·3	−17·5	−15·8	−15·6	108·2	−883·4	−9·5
	b.	23·53	23·53	24·35	24·35	22·69	21·13	21·18	15·52	404·4	20·85
	n.	·479	·479	·477	·477	·478	·457	·456	·540	·204	·455
C 2.	Temp. °Abs.										
	273	·0	−·2	·3			−·2		·1		·1*
	373	·0	−·1	·1	·0	·2	−·2	·3	−·7	1·5	·0
	473	−·1	−·1	−·1	·0	·1	·1	·2	·0	−·5	·1
	573	−·1	·0	−·1	·0	·0	·2	−·3	·1	−·7	−·1
	673	·0	·0	−·1	·0	−·3	·1	·1	·2	·0	−·1
	773	·1	·2	−·1	·0	−·1	·1	·1	·2	1·2	·0
	873	·0	·2	·1	·0	−·2	·1	·3	−·2	1·4	(2·2)
	973	·2	·3	·2	·2	·0		−·5		·1	
	1073		·0	·0	−·1	−·2		−·3		−·3	
	1173		−·2	·0	−·2	·1		−·1		−1·4	
	1273		−·5	−·1	−·2	·8		·4		−1·3	

* This is the value for 287·5° abs.

Tables D 1 & D 2.—Formula $V = b(T + a)^n$

D 1.	Constants.	Air.		Nitrogen.		Oxygen.	Carbon Di xide.		Methane.	Steam.	Nitrous Oxide.
		D , C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.	S.	S.
	a.	−3·3	−3·3	−2·8	−2·8	−5·6	−9·	−4·	63·	−145·	3·8
	b.	21·38	21·36	21·73	21·73	20·34	18·80	18·65	24·83	61·32	18·41
	n.	·49	·49	·49	·49	·49	·47	·47	·49	·375	·47
D 2.	Temp. °Abs.										
	273	−·2	−·3	−·2			−·1		−·2		−·4 *
	373	·0	·1	·0	·0	−·1	−·1	−·1	−·5	1·8	−·1
	473	·1	·3	·0	·2	·0	·1	·1	·2	−1·6	·2
	573	·1	·4	·2	·4	·1	·1	−·3	·3	−1·6	·0
	673	·2	·5	·2	·4	−·1	·0	·2	·2	−0·4	·0
	773	·2	·6	·2	·4	·2	−·1	·3	·2	1·4	·1
	873	·1	·6	·3	·3	·0	−·2	·4	−·2	1·9	(2·0)
	973	·1	·6	·3	·4	·2		−·3		·7	
	1073		·2	0	·0	·0		−·2		·2	
	1173		−·2	−·2	−·3	·2		−·1		−1·2	
	1273		−·6	−·4	−·4	·8		·3		−1·6	

* This is the value for 287·5° Abs.

Tables E 1 & E 2.

Formula $V/\sqrt{T}=b+cT^n$. $\left(V=b\sqrt{T}/(1-\frac{c}{b}T^n)\right.$ for Air, Nitrogen, Oxygen, and Carbon Dioxide.$\left.\right)$

D 1.	Constants.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide.		Methane.
		D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.	D., C. & P.
	b.	20·142	20·127	20·488	20·496	19·069	15·966		22·470
	c.	$-2{\cdot}23\times10^{-4}$	$-2{\cdot}16\times10^{-4}$	$-2{\cdot}32\times10^{-4}$	$-2{\cdot}38\times10^{-4}$	$-1{\cdot}29\times10^{-4}$	$-9{\cdot}443\times10^{-3}$		181·5
	n.	1	1	1	1	1	·637		−·705
D 2.	Temp. °Abs.								
	273	·0	−·2	·0			·0		·5
	373	·1	·1	·1	·0	·0	·0		−·5
	473	·0	·1	−·1	·0	·1	·1		·0
	573	−·1	·1	·0	·0	·1	·0		·1
	673	·0	·0	−·2	−·1	−·1	−·1		·1
	773	·0	·2	−·1	·0	·0	·0		·2
	873	−·1	·2	·0	·0	−·2	·0		·0
	973	·1	·2	·2	·2	−·1			
	1073		·0	·0	·0	−·3			
	1173		−·2	·0	−·1	−·1			
	1273		−·3	·1	·1	·5			

In the formula of Type C, to represent the results for steam, it is seen that the index of T, viz. ·204, differs considerably (as do the values of the other constants) from those found for the other two triatomic gases. This is to be expected, in view of the anomalous behaviour of steam shown by the relation between the specific heat at constant volume and temperature (see Shilling[3a]), or by a plot of $V/\sqrt{T}$ against T, in which the values of $V/\sqrt{T}$ are seen to rise to a maximum and subsequently decline.

Value of the Constant n.

A consideration of the value of n in Table B 1 seems to suggest that the deviation from ·5 (the value predicted on elementary theory, and correct for a monatomic gas obeying Boyle's law and having a constant $\gamma=1\frac{2}{3}$) is related to the molecular complexity of the gas. This is confirmed in Table C 1, where the difference is ·022 for a diatomic gas and twice that amount for a triatomic.

The variation of velocity over a considerable range of temperature does not appear to have been investigated for other gases. From the results over a restricted range for ether vapour, pentane vapour, ammonia gas, and ethylene, obtained by Dixon and Greenwood *, values of n cannot be determined with sufficient accuracy to test whether they follow this simple law.

To test the validity of formulæ C and E beyond the range 0° to 1000° C., Table F was constructed. In this table are shown the results of calculating the velocity of sound in the gases at 2000° C.: (*a*) by the formulæ proposed, and (*b*) by substituting in $V^2=\gamma RT/m$ the data given by Partington and Shilling in their book (pp. 28 & 204). The experimental values of γ at 2000° C., based as they are upon Siegel's recalculation of Pier's results for the specific heat at constant volume obtained by the explosion method, are hardly known

* Proc. Roy. Soc. A. cv. p. 199 (1924).

Values for ethane and nitrous oxide (in tubes) are given in Dixon's first paper.

Results have been obtained by tube methods for other gases by various experimenters who do not appear to have specifically tabulated comparative values of velocity, but more usually half wave-lengths. References to, and critical summaries of these investigations and earlier work over larger temperature ranges will be found in 'The Specific Heats of Gases,' by Partington and Shilling.

to the same degree of accuracy as are the values at lower temperatures.

TABLE F.

Method of Calculation.	Air.		Nitrogen.		Oxygen.	Carbon Dioxide.	
	D., C. & P.	P. & S.	D., C. & P.	P. & S.	P. & S.	D., C. & P.	P. & S.
By formula C.....	939·9	939·7	955·4	955·5	895·1	706·7	703·1
„ „ D.....	936·1	936·2	951·7	951·4	895·2	699·3	—
From $V^2=\gamma RT/m$...	921·9		937·5		877·3	709·2	

The discrepancies between the values calculated from the formulæ C and E and from $V^2=\gamma RT/m$ are too great to be accounted for by the fact that at 2000° C. the gases are ideal, whereas they are not at the lower temperatures for which the formulæ hold.

From these results it would appear that the velocity increases less rapidly with temperature over the range 1000° to 2000° C. than from 0° to 1000° C. for the diatomic gases. With carbon dioxide the agreement between the three formulæ appears better. The values calculated from formulæ C and E are in reasonable agreement with each other.

To sum up. A formula of Type C, viz. $V=a+bT^n$, appears to be of some interest in that the values of the constants obtained from both sets of results for the same gas are in good agreement, and the value of n appears to be connected with the complexity of the molecule of the gas. It is to be noted that the results considered are experimental, and do not depend for their validity upon an equation of state.

In conclusion, I wish to record my indebtedness to Prof. C. H. Lees, F.R.S., for helpful criticism during the preparation of this paper.

CXXIV. *The Surface Tension of Liquid Metals.*—Part II. *The Surface Tension of Bismuth, Cadmium, Zinc, and Antimony.* *By* L. L. Birgumshaw, *B.A., M.Sc.* (*from the National Physical Laboratory*) *.

IN a previous communication † an experimental method for the determination of the surface tension of molten metals has been described, and the results for tin and lead from the temperature of the melting-points to 1000° C. have been recorded. The method depends on the measurement of the pressure developed in a bubble of an inert gas when blown from two tubes of known radii which are immersed to the same depth in the metal. The special advantages which this method possesses in the case of molten metals were discussed. The present communication deals with the determination of the surface tension of bismuth, cadmium, zinc, and antimony with the same apparatus.

Purity of the metals used.—The bismuth contained traces of copper, iron, and lead ; the zinc 0·034 per cent. cadmium, 0·008 per cent. iron, 0·006 per cent. lead, and a trace of copper. The antimony contained 0·030 per cent. of lead, 0·001 per cent. of iron, 0·016 per cent. of copper, and a trace of nickel ; and the cadmium a trace of zinc. Four different tubes were used in the present work, and their dimensions as measured in the Metrology Department of the Laboratory are given in the following table :—

	External diameter of outer tube.	Internal diameter of outer tube.	External diameter of inner tube.
No. 1	1·120 cm.	0·920 cm.	0·1016 cm.
No. 2	1·110 „	0·910 „	0·1355 „
No. 3	0·954 „	0·842	0·1045 „
No. 4	1·012 „	0·895 „	0·1094 „

Considerable difficulties were experienced with zinc and cadmium, and it was found that, owing to the great volatility of these metals, reliable results could not be obtained with zinc above 700° or with cadmium above 600°. An alundum pot 24 cm. high was used in these cases. It was also found that in the case of zinc it was impossible to obtain any agreement between duplicate readings below 600°. It has been noticed by Evans and Richards ‡ that the rate of reduction of zinc oxide by hydrogen falls off rapidly below

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.
† Phil. Mag. ii. p. 341 (1926).
‡ Journ. Inst. Met. xxxv. p. 173 (1926).

this temperature. It may be possible that the precautions taken did not entirely prevent the entry of traces of oxygen and water-vapour, and that below 600° the hydrogen is ineffective in reducing the oxide, which may thus foul the end of the tube.

The results are given in Table I. The pressures P are given in centimetres of water, and the densities of bismuth, cadmium, and zinc have been obtained by extrapolating the

TABLE I.

Bismuth.

Temperature.	P. wide.	P. narrow.	a^2 (cm.)^2.	γ dynes/cm.
Tube 1.				
300°	13·25	23·2	0·0779	388
400	13·4	23·25	0·0782	380
600	13·8	23·2	0·0775	367
802	14·05	23·0	0·0767	353
962	14·3	22·8	0·0754	340
Tube 2.		Zinc.		
600	19·0	36·05	0·2499	787
700	19·0	35·50	0·2463	763
Tube 3.		Cadmium.		
330	18·7	34·95	0·1452	570
350	18·8	35·45	0·1488	583
374	18·9	35·85	0·1516	592
400	18·95	36·10	0·1536	597
500	19·1	36·05	0·1541	592
600	19·3	36·05	0·1545	585
Tube 3.		Antimony.		
640	14·1	23·4	0·1093	348
675	14·15	23·5	0·1102	350
700	14·25	23·6	0·1106	350
800	14·35	23·65	0·1123	348
974	14·5	23·6	0·1110	342
Tube 4.				
640	15·35	23·85	0·1100	350
700	15·45	23·9	0·1103	348
800	15·55	23·9	0·1105	346
970	15·65	23·9	0·1111	342

data given by Hogness*. The values of the density for antimony are those given by Sauerwald †.

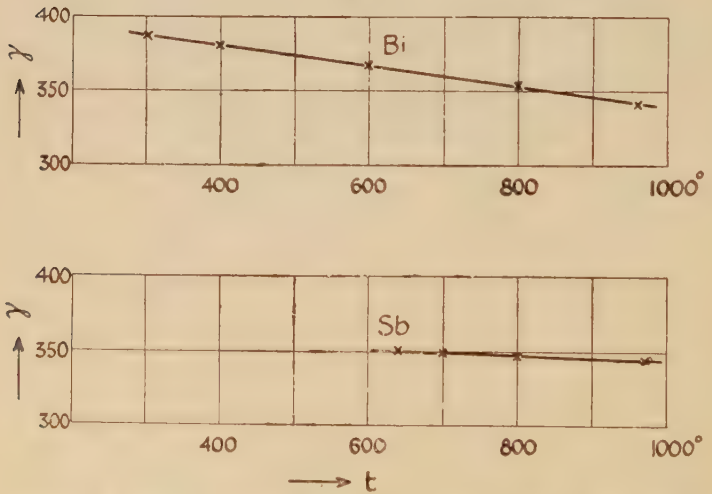
The method of calculation used is the same as in the previous paper. The specific cohesion a^2 of the metal is calculated from the formula :

$$a^2 = \frac{H}{\frac{1}{X_1} - \frac{1}{X_2}},$$

where H is the difference between the pressures (in centimetres of the metal) required to liberate bubbles from the two tubes, and X_1 and X_2 are calculated from the tables.

These results are the means of a number of determinations. In the case of antimony it was noticed that sometimes a number of readings (agreeing among themselves) were obtained which were 20 per cent. lower than the others. This low reading corresponds with a surface tension of 272 dynes/cm. and there is a possibility that this may be the correct figure, but it is unlikely. Determinations were

Fig. 1.



repeated using another tube (4), when the high results were confirmed to less than 1 per cent., the low result being obtained in only one isolated reading. It was thought that the formation of traces of stibine might interfere; nitrogen purified by passing the gas over hot copper was therefore used instead of hydrogen, but it was found to be impossible

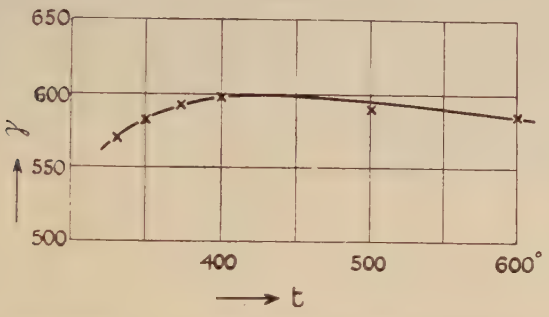
* Journ. Amer. Chem. Soc. xliii. p. 1621 (1921).

† *Zeit. f. Metallkunde*, p. 255 (1922).

to obtain any agreement in the readings, presumably owing to traces of oxygen left in the gas.

The results for bismuth and antimony are shown graphically in fig. 1, and it is seen that the surface tension is a linear function of the temperature in both cases. The curve for cadmium is shown in fig. 2. Hogness in his paper remarks that "the surface tension of cadmium appears to go through a maximum." This remarkable result has been definitely confirmed in the present work, and apparently liquid cadmium is the only pure liquid known in which the surface tension rises with rise of temperature.

Fig. 2.



A comparison of the present results with those of previous workers is given in Table II. (The temperatures are given in brackets.)

TABLE II.

	Bismuth.	Zinc.	Cadmium.	Antimony.
Quincke	465	967	815	317
Siedentopf ...	429	—	830	—
Smith	346 (700–850°)	707 (580–630°)	—	274 (840–850°)
Hogness	375 (320°)	753 (477°)	622 (421°)	
Author	388 (300°)	787 (600°)	600 (425°)	350 (640°)

The results at low temperatures agree very well with Hogness with the exception of the values for zinc, which appear to be about 5 per cent. higher. In view of the troubles experienced at temperatures below 600°, the present results may be distinctly high. The value for cadmium at the maximum (425°) is slightly lower (3 per cent.) than the value given by Hogness.

Since the commencement of the present work, a communication has appeared by Sauerwald and Drath (*Zeit. Anorg. Chemie*, June 1926, p. 79) on the surface tensions of

mercury and bismuth. The value found for the latter metal at 583° is 353·9 dynes/cm.

Sugden * has shown that the expression $\frac{\gamma^{\frac{1}{4}}}{D-d}$ (where D is the density of the liquid and d that of the vapour) is constant for a large number of non-associated liquids over large ranges of temperature. In the case of liquids usually regarded as associated this "constant" increases slowly with rise of temperature, and in the previous communication (*loc. cit.*) it was found that for tin and lead from their melting-points to 1000° this expression increased about 5 per cent. Its value has been calculated for bismuth, cadmium, and antimony (Table III.), and in each case found to rise. In the case of bismuth, where the temperature range is roughly the same as in the case of tin and lead, the increase is again 5 per cent. The results are shown graphically in fig. 3, and it is seen that this function is either linear with increase of temperature or slightly convex to the temperature axis.

Table III.

t.	γ.	D.	$\frac{\gamma^{\frac{1}{4}}}{D}$.
Bismuth.			
300°	388	10·03	0·442
400	380	9·91	0·445
600	367	9·66	0·453
802	353	9·40	0·461
962	340	9·20	0·468
Cadmium.			
330	570	8·01	0·610
350	583	7·99	0·615
374	592	7·96	0·620
400	597	7·93	0·623
500	591	7·82	0·630
600	585	7·72	0·637
Antimony.			
640	350	6·49	0·663
700	349	6·45	0·670
800	346	6·38	0·676
970	342	6·29	0·682

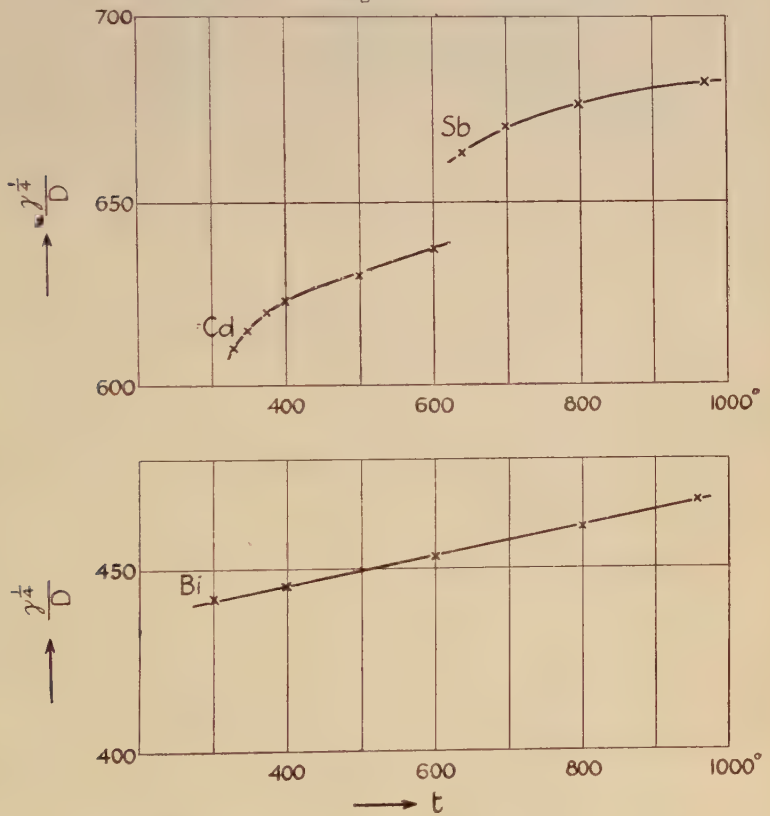
* Trans. Chem. Soc. cxxv. p. 32 (1924); *ibid.* cxxv. p. 1167 (1924).

In the well-known formula for the temperature coefficient of molar surface energy,

$$\frac{d}{dt}\left\{\gamma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}\right\} = K,$$

K is found to be approximately $-2{\cdot}2$ for a number of unassociated liquids. Very few calculations of this constant appear to have been made for molten metals.

Fig. 3.



Harkins and Ewing * find K to be $-0{\cdot}96$ for mercury. In the present case K has been calculated from the simple formula :

$$\frac{\gamma_1\left(\frac{M}{\rho_1}\right)^{\frac{2}{3}} - \gamma_2\left(\frac{M}{\rho_2}\right)^{\frac{2}{3}}}{T_1 - T_2},$$

* Journ. Amer. Chem. Soc. xlii. p. 2539.

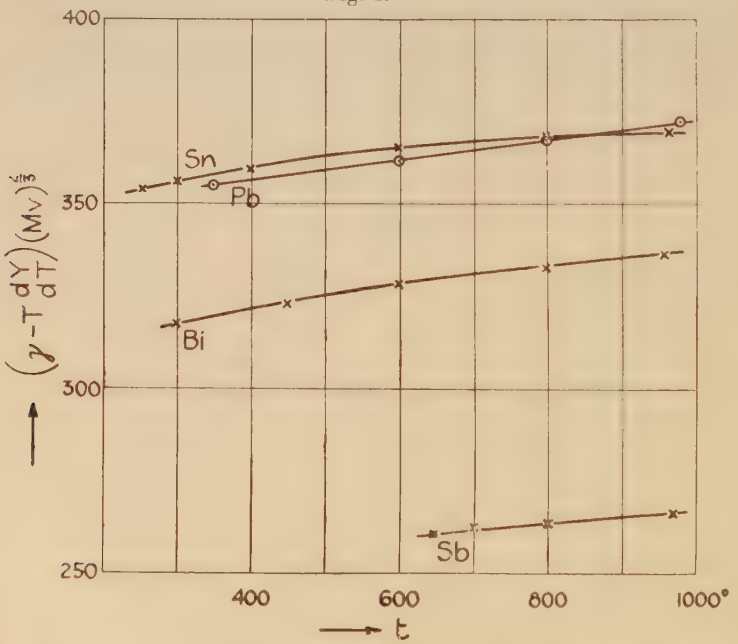
and the results are given in Table IV. T_1 and T_2 are the limits of temperature for which the surface tension was determined.

TABLE IV.

	K.
Tin	0·10
Lead	−0·22
Bismuth	−0·27
Cadmium (330°–425°) . .	2·15
Cadmium (425°–600°) . .	−0·20
Antimony	−0·02

With the exception of cadmium (330–425°), these values of K are very low.

Fig. 4.



Bennett and Mitchell *, in an investigation on the surface tensions of a large number of organic liquids, found that the molar total surface energy $\left(\gamma - T\frac{d\gamma}{dT}\right)(Mv)^{\frac{2}{3}}$ was a constant for a large number of unassociated liquids, while for liquids usually regarded as associated this

* *Zeit. Phys. Chem.* lxxxiv. p. 475 (1913).

"constant" increased with increase of temperature. In Table V. this function has been calculated for these

TABLE V.

Temperature.	$\left(\gamma - T\frac{d\gamma}{dT}\right)$.	$\left(\gamma - T\frac{d\gamma}{dT}\right)(Mv)^{\frac{2}{3}}$.
Tin.		
253°	535	3536
299	537	3561
401	537	3590
600	540	3648
800	538	3680
964	535	3693
Lead.		
350	491	3553
400	488	3538
600	490	3610
800	491	3673
982	491	3724
Bismuth.		
300	421	3176
400	424	3224
600	424	3279
802	423	3332
962	420	3359
Cadmium.		
330	62·8	365·4
350	2?9	1510
374	385	2249
400	476	2787
425	600	3203
500	657	3885
600	660	3934
Antimony.		
640	372	2605
700	373	2619
800	372	2634
970	372	2663

metals, and the total surface energy is also given. It is worthy of note that here again, as in the case of the function $\frac{\gamma^{\frac{1}{4}}}{D}$, the increase in the case of tin, lead, and bismuth is approximately 5 per cent. The results are shown graphically in fig. 4.

A change is thus found both in McLeod's "constant" and in Bennett and Mitchell's which is comparable with that obtained for associated liquids over a much greater range of "reduced" temperature. If, therefore, the constancy of these relations is accepted as a criterion of an unassociated liquid, then it appears that tin, lead, bismuth, cadmium, and antimony are all associated in the liquid state.

Summary.

The surface tensions of liquid bismuth, cadmium, zinc, and antimony have been determined.

The surface tension of cadmium passes through a maximum at 425°.

Evidence is brought forward to show that bismuth, cadmium, and antimony may be highly associated in the liquid state.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his interest during the progress of this work, and Mr. J. Trotter for assistance in the experimental portion.

CXXV. *The Process of Quantization.* *By* G. P. Thomson, *M.A., Fellow of Corpus Christi College, Cambridge, and Professor of Natural Philosophy in the University of Aberdeen, and* Ronald G. J. Fraser, *B.Sc., Ph.D.*, 1851 *Exhibition Senior Student* *.

Summary.

It seems inherently probable, when the motion of an atom in a stationary state is interrupted by collision or otherwise, that the subsequent adjustment of the system towards a condition satisfying the quantum postulates takes a finite time.

This idea can be used to erect a correspondence between

* Communicated by the Authors.

the broadening of a spectral line due to pressure, on the classical and quantum theories; and from this we may derive a good deal of information about the way in which quantization is approached. It is also shown to be in agreement with the experimental results of Fuchtbauer and Joos on pressure broadening.

Introduction.

THE criteria by which the stationary states of an atomic system are selected from the continuous manifold of states presented by the classical theory involve the assumption of periodic motion of the system in the stationary state. Now no motion is truly periodic unless it persists indefinitely; while the actual atomic motion is supposed to be liable to interruption, either spontaneously or by transitions induced by radiation or collision. There is thus an approximation involved in the hypothesis of rigorously periodic states, and the extent to which the actual state differs from the ideal may be termed the diffuseness of the quantization. This idea, originally introduced by Bohr *, has recently been discussed by several writers † from various viewpoints—the present paper constitutes an attempt to approach the matter from what we believe to be a new angle.

The particular form of interruption of the atomic motion which we propose to discuss is that due to the collisions with other atoms considered in the kinetic theory. The present theory will therefore apply directly only to gases at sufficient densities for these collisions to be the most important cause of interruption; but the conclusions which it is possible to draw as to the rate at which quantization occurs refer to the behaviour of atoms in the intervals between collisions, and thus must hold independent of the density.

Now these collisions will, on the classical theory, limit the length of the coherent wave-train emitted by an atomic oscillator, and hence its homogeneity. Thus a spectral line will appear broadened to an amount depending on the frequency of collisions, *i. e.*, on the pressure of the gas. As will be seen below, the observed broadening at high pressure is in agreement with that calculated on these lines.

* *Cf.* Proc. Camb. Phil. Soc, Supplement (1924); also *Naturwiss.* xii. p. 1115 (1924).

† Ehrenfest & Tolman, Phys. Rev. xxiv. p. 287 (1921); Slater, *ibid.* xxvi. p. 419 (1925); Landé, *Zeit. Phys.* xxxv. p. 317 (1925).

If we assume that the correspondence principle applies for these phenomena, the quantum theory must predict an equal broadening, at least in the case where large quantum numbers are involved. If we keep the law that the frequency of radiation is proportional to the energy in a quantum, we must suppose the energy in the quantum to vary, and hence transitions to occur between energy levels other than the normal. This implies that the quantization is diffuse. In fact, we may argue thus :—The Correspondence Principle may be taken in the form that the chance of a transition involving a change of α_k in the quantum number n_k is proportional to the (amplitude)^2 of the α harmonic in the Fourier series for $\ddot{q}_k$. For fractional changes of quantum number this naturally becomes that the chance of a quantum leap $\alpha_k+\epsilon$ is proportional to the intensity of that part of the Fourier series whose frequency differs from that of the α harmonic by p, where $p=\epsilon\nu_k$, and ν_k is the frequency of the fundamental. If we write this intensity as $\psi_{\alpha k}(p)\,dp$, then the chance of a quantum leap is $\psi_{\alpha k}(\epsilon\nu_k)\,\nu_k d\epsilon$.

The shorter the time between collisions the wider will the line be on the classical theory, and hence the greater will the chance be of the quantum number changing by a fractional amount. But such changes can only occur if one at least of the states between which the transition occurs is abnormal, *i. e.*, the quantization is diffuse. We are thus led to the result that "*the pressure broadening of spectral lines implies the existence of diffusely quantized orbits*," and the higher the pressure the more diffuse they will be on an average.

It has been suggested by L. de Broglie *, and in another form by one of the authors †, that a quantized orbit is one in which the orbit is in tune with some accompanying vibration. On this view it is natural to interpret the above result as meaning that the orbits start at random and are gradually forced into the "stationary" states. The quantization is thus at first non-existent (or infinitely diffuse) and becomes sharper and sharper with the lapse of time as the previously diffusely quantized states cluster more and more closely about the positions in the qp phase space corresponding to the fully quantized motions. It should be emphasized that such a result is *statistical* only ; nothing can be said on

* Phil. Mag. [6] xlvii. p. 446, and later papers.
† Phil. Mag. [6] l. p. 163 (1925).

the basis of the correspondence principle as to the behaviour of a single atom *.

Before considering the mathematical theory in detail, it may be well to show that the general idea of pressure broadening by interrupting the periodicity of the atoms is in agreement with experiment.

Comparison with experiment.—The broadening of spectral lines under pressure is a familiar effect, and has been investigated by many experimenters. Unfortunately most of them have worked with the vapours of the alkali metals, which appear to be abnormal in that the broadening is probably connected with the formation of unstable molecules.

Füchtbauer and Joos† have, however, examined carefully the broadening of the mercury absorption line 2537—the pressure, of many atmospheres, being exerted by a neutral gas so that the chance of chemical action is minimised. In these conditions they find that the broadening is proportional to the density for hydrogen and nitrogen. This agrees with our theory if the temperature is kept constant, as it appears to be approximately. For CO_2 they found the broadening varied as the 2/3 power of the density. Only three points, including zero, are, however, shown, and the divergence from a straight line hardly appears to exceed the experimental error. The temperature also is not recorded in all cases‡. Füchtbauer and Joos take as the measure of the width of a line the distance between the points at

* We would wish to emphasize the *statistical* nature of this result, inasmuch as Landé (*loc. cit.*) has suggested that the width of a spectral line arises from the indefiniteness of every transition. Thus *each* atom would emit a spectral band instead of a line. Landé, however, is concerned with that part of the width caused by the finite time of emission, while we are concerned with the breadth due to the interruption of the radiation by collisions—a pressure effect. The two views are not therefore incompatible. Nevertheless, while admitting that the radiation from even a single atom cannot be strictly monochromatic, since it does not last for ever, we prefer to ascribe this width to effects occurring outside the atom after emission, the act of radiation being primarily the emission of energy which then generates (approximately) monochromatic waves of frequency proportional to the energy. The degree of homogeneity for each atom would in such case be governed by considerations quite different from those dealt with here; *e. g.*, it might depend on the distance between the points of emission and absorption.

† *Phys. Zeit.* xxiii. p. 73 (1922).

‡ *Note added in proof.*—In *Ann. der Physik*, lxxi. p. 208, Füchtbauer, Joos, and Dinkelacher give a fuller account of their experiments. More numerical data are given, which do not, however, differ substantially from the examples shown in the table. They find also that carbon dioxide, like the other gases, gives a breadth proportional to the density.

which the intensity is half the maximum. The width of the line as thus defined can be calculated on the above theory as follows. On our theory, the places where the intensity is half the maximum can be shown from equation (2), below to be the places where $T.p=\cdot 443$ and T is the mean free path divided by the velocity of mean square.

Gas	Hydrogen.	Nitrogen.	Carbon Dioxide.
Pressure, in atmospheres ...	30	50	25·1
Temperature	34·5°	37·5°	38·5°
T (calculated from data in Kaye and Laby, p. 33.) (In secs.)	$3{\cdot}5\times10^{-12}$	$4{\cdot}08\times10^{-12}$	$6{\cdot}85\times10^{-12}$
$2p=\frac{\cdot 886}{T}$ (sec.$^{-1}$)	$2{\cdot}52\times10^{11}$	$3{\cdot}16\times10^{11}$	$1{\cdot}30\times10^{11}$
Observed width (sec.$^{-1}$) ...	$3{\cdot}2\times10^{11}$	$3{\cdot}8\times10^{11}$	$1{\cdot}4\times10^{11}$

The last line gives the observed width, corrected for the width of the slit and expressed in frequency difference. It will be seen that observed and calculated values are of the same order, but the former somewhat smaller. This is probably due to two causes. In the first place, the approximation of regarding all intervals between collisions as equal is bound to give an underestimate of the width. In the second place, Füchtbauer and Joos find that in nitrogen and carbon dioxide the broadening is unsymmetrical, being greater towards the red. This is probably connected with the pressure shift of the line, which is most marked in these gases, and is probably due to some different cause from that considered above, *e. g.*, the influence of stray molecular fields. It should be noticed that the agreement between theory and experiment is best in hydrogen, which does not show this unsymmetrical effect.

We will now proceed to develop the above theory in detail, and to show that consistent laws can be found for the rate at which a group of atoms, with orbits originally diffusely quantized, approach the normal stationary state.

On the classical theory, the phase of an oscillator is changed by collision so that the trains of waves emitted before and after a collision are not fully coherent. The general expression for the distribution of the intensity of a spectral line arising from this cause has been investigated by Godfrey * and by Rayleigh †. The general result is complicated by several factors. In the first place, there is

* Godfrey, Phil. Trans. A, vol. cxcv. p. 329 (1901).
† Rayleigh, 'Scientific Papers,' vol. v. p. 257.

in general some degree of persistence of phase—somewhat analogous to the persistence of velocities, especially if the energy of impact is less than the energy of the oscillator. Next, account must be taken of variations in the free path and velocity of the colliding particles. We shall neglect the possibility of any persistence of phase—a neglect which probably does not greatly affect the generality of the result—and start from the first approximation, in which all the free paths are taken as being the same and the velocity as constant and equal to the root mean square velocity.

The radiation from any atom will be represented by $A \sin 2\pi\nu t$, but the expression is only valid over the range $0 < t < T$, where T is the interval between collisions. Thus the radiation emitted is not truly monochromatic, but may be analysed into a Fourier series such that the intensity between p and $p+\delta p$ is

$$\frac{C \sin^2 \pi . T . p}{\pi^2 T^2 p^2} . \delta p, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $p+\nu$ is the frequency. This first vanishes when $p = 1/T$, and is small afterwards (being, in fact, the familiar expression for the intensity in the diffracted image of a slit). In the more accurate investigation, when variations in free path are considered, there is no zero, and the intensity continually diminishes as p increases. In what follows we will take as an approximation to the complicated expression that arises when all the varying quantities are fully considered, the simple form:

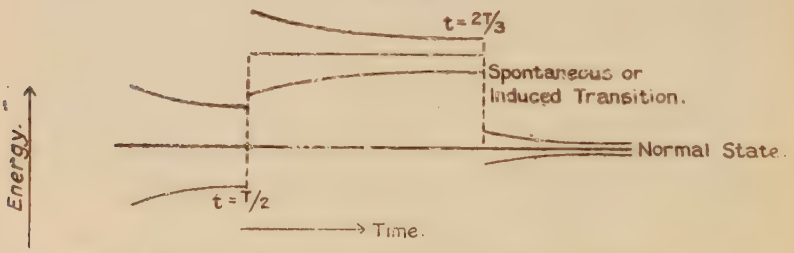
$$C e^{-3 \cdot 5 T^2 p^2} \delta p, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which continually diminishes as p increases, makes, in agreement with (1), the half-width of the line vary inversely as T, and whose graph follows very closely that of (1) except for the absence of zeros. The exact value of the constant is chosen so that (1) and (2) intersect where the ordinate is half the maximum. This is to facilitate comparison with the experimental results. We have shown that the chance of a transition involving a change of quantum number $\alpha + \epsilon$ must follow a law closely connected with the above. In fact, $\psi(p)\delta p = C e^{-3 \cdot 5 T^2 p^2} \delta p$ and the chance in question, $\psi(\epsilon\nu_k)\nu_k \delta\epsilon$, is $C e^{-3 \cdot 5 T^2 \nu_k^2 \epsilon^2} . \nu_k \delta\epsilon$. Clearly the chance of a transition involving the fractional change ϵ will be closely connected with the proportion of the orbits whose quantum numbers differ from integers by ϵ, but the exact

nature of the connexion requires further assumptions as to the effects of the emission and absorption of radiation.

In accordance with the fundamental idea, we suppose the atomic orbits thrown into confusion by each collision and gradually returning to the stationary states when left alone. The conditions under which a transition occurs are thus dependent on the time since the last collision. Now suppose that T, the interval between collisions, is small compared with the time in which half the atoms in an aggregate would undergo transitions, either spontaneous or induced by radiation ; in other words, that T is less than the time of excitation of the atoms. At atmospheric pressure, T is of the order 10^{-10} sec. and the time of excitation has been found by various observers to be of the order 10^{-8} sec. ; so that for the present discussion of pressure broadening of spectral lines the condition is satisfied. With this restriction, if the chances of the occurrence of a transition depended *only* on the radiation density and were independent of the time since the last collision, the average time at which a transition would occur is T/2.

Fig. 1.



If, on the other hand, we suppose that a collision reduces an atom to the normal state, it must absorb radiation before it can re-emit. The average time for absorption of radiation is T/2, so that the time for re-emission averages 2T/3. This will be clear from an examination of fig. 1. Thus the mean time at which a transition occurs is in either case a fraction of T and proportional to it.

It should be noticed that we have here the definite assumption that the energy of the diffusely quantized states changes with the time. One cannot see that an atom is prevented from emitting or absorbing energy if it is not in a fully quantized state. One may perhaps be permitted to imagine an energy interchange taking place between states approximating to the n-quantum state for which ϵ is negative on the one hand and positive on the other.

In order to preserve symmetry between the initial and final states it is necessary to assume that, alike in absorption and in radiation, a group of atoms which are diffusely quantized before a transition are also diffusely quantized afterwards. This introduces an uncertainty in the change of quantum number even for an atom for which ϵ is known before the transition.

We shall now show that for non-degenerate orbits of n degrees of freedom, if we define $f_k(\epsilon)$ to be a function such that $f_k(\epsilon)\delta\epsilon$ is the fraction of atoms for which the quantum number k has a value differing from an integer by ϵ, then

$$f_k(\epsilon) = \nu C' e^{-3\cdot5t^2\nu^2\epsilon^2\kappa}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where κ is a constant to be determined. The value of C′ can be found at once, since

$$\int_{-\infty}^{\infty} f(\epsilon)\, d\epsilon = 1.$$

Hence

$$C' = \frac{t\sqrt{3\cdot5\kappa}}{\sqrt{\pi}}.$$

The time t is measured from the last collision.

Consider a frequency

$$\Omega = | \ \tau_1\nu_1 + \tau_2\nu_2 + | \ldots | \ .$$

On the classical theory the amplitude at p is $Ce^{-3\cdot5T^2p^2}\delta p$, which depends only on T and p.

From the dynamical theory of orbits it is known that $\nu_k = \dfrac{\partial H}{\partial J_k}$, where H is the energy and J_k is an action integral. Therefore for large quantum numbers the change in energy in the transition is

$$\Delta H = h(n_1 - n_1')\nu_1 + h(n_2 - n_2')\nu_2 + \ldots,$$

where $n_1, n_2 \ldots$; $n_1', n_2', \ldots$ are the quantum numbers before and after the transition.

For strict quantization

$$\Delta H = h\tau_1\nu_1 + h\tau_2\nu_2 + \ldots$$

Thus the change in ΔH due to the quantization being diffuse is

$$h(\epsilon_1 - \epsilon_1')\nu_1 + h(\epsilon_2 - \epsilon_2')\nu_2 + \ldots;$$

$$\therefore \quad p = \Sigma(\epsilon_1 - \epsilon_1')\nu_1.$$

Now the amplitude at p is the chance of $\Sigma(\epsilon_1-\epsilon_1')\nu_1$ lying between p and $p+\delta p$. The chance of $\epsilon_1\nu_1$ lying between $\epsilon_1\nu_1$ and $\epsilon_1\nu_1+\delta$ is

$$f(\epsilon_1)\delta/\nu_1=\delta\,.\,\frac{t\sqrt{3\cdot5\kappa}}{\sqrt{\pi}}\,.\,e^{-3\cdot5t^2\nu_1{}^2\epsilon_1{}^2\kappa}. \quad . \quad . \quad . \quad (4)$$

At the time of transition t is a fraction of T, which we will write ηT, and the chance is

$$\delta\,.\,\frac{\eta\,.\,\mathrm{T}\,.\sqrt{3\cdot5\kappa}}{\sqrt{\pi}}\,.\,e^{-3\cdot5\eta^2\mathrm{T}^2\nu_1{}^2\epsilon_1{}^2\kappa},$$

which may be written $\delta\,.\,\phi(\nu_1\epsilon_1)$, the other quantities involved in ϕ being constants.

Take new variables

$$(\xi_1,\,\xi_2,\,\ldots\,\xi_1',\,\xi_2'\ldots)=(\nu_1\epsilon_1,\,\nu_2\epsilon_2,\,\ldots\,-\nu_1\epsilon_1',\,-\nu_2\epsilon_2'\ldots).$$

Then in the $2n$-dimensional space whose coordinates are $\xi_1,\ldots\xi_1'$ each pair of initial and final conditions of the atom is represented by a point. Also the form of the function $\phi(\xi)$ shows that these points are distributed with spherical symmetry about the origin, assuming that the chance of an assigned value of any ξ is independent of the values of the remainder. The chance of $\Sigma(\xi_1+\xi_1')$ lying between p and $p+\delta p$ is the number of points between the planes $p=\Sigma(\xi_1+\xi_1')$ and $p+\delta p=\Sigma(\xi_1+\xi_1')$, From the symmetry this is

$$\phi(p/\sqrt{2n})\,.\,\delta p/\sqrt{2n}\,.\int_{-\infty}^{\infty}\!\!\int\!\!\int\!\!\int\phi(\xi_2)\ldots\phi(\xi_n)\phi(\xi_1')\ldots\phi(\xi_n')d\xi_2\ldots d\xi_n\,d\xi_1'\ldots d\xi_n'$$
$$=\phi(p/\sqrt{2n})\,.\,\delta p/\sqrt{2n}.$$

Therefore the amplitude at p is

$$\mathrm{D}\phi(p/\sqrt{2n})\,.\,\delta p/\sqrt{2n}=\frac{\mathrm{D}'}{\sqrt{2n}}\,.\,e^{-3\cdot5\eta^2\,.\,\mathrm{T}^2\,.\,p^2\,.\,\kappa/2n},$$

where D depends on the probability of the transition. This agrees with the form found on the classical theory ($e^{-3\cdot5\mathrm{T}^2p^2}$ if $\mathrm{D}'=\mathrm{C}\sqrt{2n}$ and $\kappa=2n/\eta^2$, which is a constant in agreement with the assumption. Hence

$$f(\epsilon_k)=\frac{\nu_k t\sqrt{7n}}{\eta\sqrt{\pi}}\,.\,e^{-3\cdot5t^2\nu_k{}^2\epsilon_k{}^2\,.\,2n/\eta^2} \quad . \quad . \quad . \quad (5)$$

for all the quantum numbers both before and after the transition.

It must be emphasized that, while the statistical distribution of orbits round the fully quantized states is unaffected by a transition, each individual orbit will (in general) have a different value of ϵ from that before the transition. Otherwise, of course, the energy difference would be practically the same, and the whole explanation would break down. If we write $\nu_k t = N$, the number of complete periods since the last collision, $f(\epsilon)$ may be written $f(\epsilon) = aNe^{-bN^2\epsilon^2}$, where a and b are constants. This form shows clearly how, as N increases, the orbits are grouped more and more closely round the values $\epsilon = 0$, *i. e.*, the fully quantized states. A measure of the diffuseness of quantization is the range of ϵ within which any arbitrary fraction (say 90 per cent.) of the orbits fall. Hence from the above expression we deduce that the diffuseness is inversely as N. Thus, whatever the period, a given number of revolutions has the same effect in making the orbits approximate to the fully quantized state.

Degenerate Cases.

Degeneration may arise either through one of the frequencies approaching zero or through a linear relation with integral coefficients occurring between the frequencies. The former case causes no difficulty. We merely have one of the degrees of freedom quantized more and more slowly as the corresponding frequency diminishes, until, finally, no quantization occurs in the time at our disposal, which is limited by the fact that the radiation in the corresponding classical case must cause no appreciable change in the orbit. (See, for example, the case of the Zeeman effect considered below.)

The other case leads to a more complicated result. It is exemplified by the degeneration into a Kepler ellipse which occurs when the radial and azimuthal frequencies become equal. In this case, looking at the matter from the point of view of the physical picture, we suppose that the two periodic forces which are moulding the orbit, being of almost the same period, interfere with each other. The result is that the simple expression for the rate of quantization breaks down.

Analytically, the case may be considered thus. Any related frequency may be written $\tau_1\varpi_1 + \tau_2\varpi_2$, where τ_1, τ_2 are integers or zero; but if $\varpi_1 = \varpi + \delta$; $\varpi_2 = \varpi - \delta$, this is $(\tau_1 + \tau_2)\varpi + (\tau_1 - \tau_2)\delta$.

This looks at first as if ϖ, δ might be taken as frequencies equally with ϖ_1, ϖ_2. But in general this is not so, for

$(\tau_1+\tau_2)$, $(\tau_1-\tau_2)$ are not *any* integers (*e. g.*, 1, 0 give $\tau_1=\tau_2=1/2$, which is not allowed). But if δ is small, the two lines ϖ_1, ϖ_2 lie near each other and will overlap. We may regard the centre of the line as of the frequency ϖ, and if ϖ is admitted as a possible frequency, the system ϖ, δ is as much entitled to consideration as ϖ_1, ϖ_2. In fact, if δ is very small compared with the width of the line, the former is the more natural, for the line appears single and of frequency ϖ. To a higher approximation it has two satellites $\varpi\pm\delta$ (unresolved). Now the width of the line is inversely as t. Thus, to begin with, δ will be "small" in the sense of the above argument; but after the lines have become so narrow that the space between them is almost completely dark, there is no frequency ϖ, and the two frequencies ϖ_1, ϖ_2 must be treated as independent. Thus initially, if ϵ_1, ϵ_2 are the values of ϵ corresponding to ϖ_1, ϖ_2,

$$f(\epsilon_1+\epsilon_2)=\frac{2\sqrt{3\cdot5}\varpi t}{\eta\cdot\sqrt{\pi}}\cdot e^{-3\cdot5t^2\cdot\varpi^2\cdot(\epsilon_1+\epsilon_2)^2\cdot4/\eta^2}$$

and

$$f(\epsilon_1-\epsilon_2)=\frac{2\sqrt{3\cdot5}\delta t}{\eta\cdot\sqrt{\pi}}\cdot e^{-3\cdot5t^2\cdot\delta^2\cdot(\epsilon_1-\epsilon_2)^2\cdot4/\eta^2}.$$

This means that $\epsilon_1+\epsilon_2$ rapidly becomes small, while $\epsilon_1-\epsilon_2$ does so much more slowly. When t is large, however, compared with $1/\delta$, we have instead

$$f(\epsilon_1)=\frac{2\sqrt{3\cdot5}\varpi_1 t}{\eta\sqrt{\pi}}\cdot e^{-3\cdot5t^2\cdot\varpi_1{}^2\epsilon_1{}^2\cdot4/\eta^2},$$

and similarly for $f(\epsilon_2)$.

Physically this means that the ellipses rapidly assume the right major axis, but take longer to pick up their excentricity. After the precession has gone through several periods, however, the radial and azimuthal quantizations proceed independently.

Diffuse Quantization in Space.

We may now extend the above ideas to include the case of diffuse quantization in space. The theories of the Stark and Zeeman effects both depend, of course, on the assumption of a discrete series of orientations of the vector of angular momentum of the atom relative to the applied field. It is easy to show that in the event when the motion in a space-quantized energy state is subject to interruption, then there is a calculable range of positions grouped around the position in space occupied by the fully quantized state, which it is permissible for the momentum vector to occupy.

Zeeman Effect.

If o be the Larmor frequency, then

$$o = \frac{1}{4\pi} . e/m . \mathrm{H/c\ sec.}^{-1},$$

where the symbols have their usual meaning.

Then the energy W is given, for a hydrogen orbit, by

$$\mathrm{W} = \frac{h}{4\pi} . e/m . \mathrm{H/c} . k(1-\cos\theta),$$

where θ is the angle which the normal to the orbital plane makes with the field direction, and k is the azimuthal quantum number. k is an integer, since the corresponding motion is to be regarded as fully quantized.

Hence, writing $k\cos\theta = n_{\mathrm{H}}$, the plane of the orbit is connected with the defect of magnetic quantum number by the equation

$$\cos\theta = \frac{n_{\mathrm{H}} \pm \epsilon}{k}$$

and the range of $\cos\theta$ is

$$\frac{n_{\mathrm{H}} \pm 1/\mathrm{N}}{k} = \frac{n_{\mathrm{H}} \pm \dfrac{4\pi . m . c}{e . \mathrm{H}} \cdot \dfrac{1}{\mathrm{T}}}{k}, \quad \text{where} \quad \mathrm{N} = o . \mathrm{T}.$$

In the general case of a non-hydrogenic atom, θ becomes the angle between the field direction and the vector of angular momentum; k is replaced by the quantum number of total angular momentum, $\bar{j}$.

Evidently the range of $\cos\theta$ is inversely as H; thus the breadth of Zeeman components should decrease with increasing field. It is doubtful if this result is capable of experimental test.

Aberdeen,
August 1926.

Note added in proof.—The above paper was mostly written in the early summer of 1926, and is based on the ideas developed by de Broglie in his earlier papers. The rapid progress of the wave theory of mechanics has modified ideas of atomic structure, and some of the phraseology of this paper is out of date. We believe, however, that the ideas involved are generally applicable, and must have a place in whatever is the final solution of the problem of radiation. In the present rapid development of the new theories it seems better to keep to the older language rather than to restate the results in new terms.

CXXVI. *Frequency Changes of Light and Quantum Theory.*

By G. Breit, *Department of Terrestrial Magnetism, Carnegie Institution of Washington, and* Arthur Edward Ruark *and* F. G. Brickwedde, *Bureau of Standards* *.

Abstract.—According to the classical wave theory of light, a monochromatic train of waves ceases to be monochromatic if it is interrupted—say by a mechanical shutter. In the above an attempt has been made to explain this result of classical theory from the point of view of quanta. Two points of view are presented. In both the important assumption is that the mechanism which interrupts the wave may contribute to the energy of the quantum passing through it.

In the first explanation (section 1) the interrupting mechanism is pictured as first absorbing and then re-emitting the quantum. On applying proper selection rules the correct frequencies are obtained.

In the second explanation the interrupting apparatus and the emitting atom are considered as one big atom (section 3).

The theory is applied to Righi's experiments on light beats (section 2). It is shown, particularly by discussing a common misconception of the case of natural light, that the theory is applicable only if phases can be considered as preserved in scattering.

1. *The Quantum Theory of Frequency Changes due to Modulation.*

IT has been shown by Schroedinger † that the Doppler effect can be interpreted from the point of view of pure quantum theory. His well-known explanation involves only the conservation of energy and momentum as applied to a Bohr atom and a unidirectional quantum. We concern ourselves here with frequency changes of a somewhat different type which result from changes in the transmission of optical apparatus. On the classical wave theory such cases are typically represented by the identity

$$2\sin 2\pi \mathrm{N}t\,.\,\cos(2\pi\nu t-\epsilon) \equiv \sin\left[2\pi(\nu+\mathrm{N})t-\epsilon\right]-\sin\left[2\pi(\nu-\mathrm{N})t-\epsilon\right].$$

This equation tells us that if monochromatic light of frequency ν is incident on a device which is capable of varying the amplitude of the transmitted wave with a frequency N, then the transmitted light consists of two

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† Schroedinger, *Physik. Zs.* xxiii. p. 301 (1922).

monochromatic waves of frequencies $\nu \pm \mathrm{N}$. More generally

$$\cos(2\pi\nu t - \epsilon)\Sigma a_n e^{2\pi i n \mathrm{N} t} = \tfrac{1}{2}\Sigma a_n \left[e^{i(2\pi(\nu + n\mathrm{N})t - \epsilon)} + e^{-i(2\pi(\nu - n\mathrm{N})t - \epsilon)} \right] \quad (1)$$

expresses the fact that a periodic change in amplitude of frequency N gives rise to frequencies $\nu \pm n\mathrm{N}$ $(n = 0, 1, 2, \ldots)$.

Just as in the case of the Doppler shift moving interferometer fringes can be used to demonstrate the effect, so in these cases Righi * showed by means of turning nicols and other devices that the effects are correctly predicted by classical wave theory. We shall consider Righi's experiments in some detail presently. First, however, some theoretically simpler cases must be discussed.

Let us consider an anisotropic oscillator attached to a large mass which is free to turn about a fixed axis. On the classical wave theory, if the direction of the axis be OZ and the incident wave be also along OZ and polarized along OX, the scattered wave along OZ is

$$\left.\begin{aligned} \mathrm{E}_x &= \mathrm{A}\cos^2 2\pi\mathrm{N}t\cos(2\pi\nu t - \epsilon), \\ \mathrm{E}_y &= \mathrm{A}\sin 2\pi\mathrm{N}t\cos 2\pi\mathrm{N}t\cos(2\pi\nu t - \epsilon), \end{aligned}\right\} \quad . \quad . \quad (2)$$

where A is a constant. It contains, therefore, the frequencies ν and $\nu \pm 2\mathrm{N}$. On pure quantum theory we assign to the oscillator a vibrational quantum number n and a rotational quantum number j. The energy of the oscillator is with a sufficient approximation

$$\mathrm{W} = nh\nu_0 + \frac{j^2h^2}{8\pi^2\mathrm{I}}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here $\mathrm{N} = \dfrac{jh}{4\pi^2\mathrm{I}}$.

In order to discuss the behaviour of the oscillator we must consider the probabilities of absorption and emission following the Correspondence Principle. If we denote the frequencies associated with n and j by ω_n and ω_j the motion of the oscillator is represented by

$$x + iy = ae^{2\pi i\omega_j t}\cos(2\pi\omega_n t - \epsilon),$$

which tells us that the selection rules

$$\Delta n = \pm 1, \quad \Delta j = \pm 1$$

apply. Hence on absorption

$$h\nu = h\nu_0 + \frac{(1 \pm 2j)h^2}{8\pi^2\mathrm{I}} \simeq h(\nu_0 \pm \mathrm{N}),$$

* *Journal de Physique* (2), p. 437 (1883).

since j is large as compared with unity. Therefore, the incident quantum is absorbed only if

$$\nu_0 = \nu \mp \mathrm{N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Quite similarly on emission a quantum ν' is sent out such that

$$\nu' = \nu_0 \pm \mathrm{N} = \nu, \nu \pm 2\mathrm{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The result agrees with the predictions of the wave theory also so far as intensities are concerned.

If circularly polarized light is incident on the model and if the sense of rotation of the oscillator is opposite to that of the light, the classical expansions are seen to be of the form

$$\left.\begin{aligned} \mathrm{E}_x &= \mathrm{A} \cos 2\pi \mathrm{N}t \cos [2\pi(\nu + \mathrm{N})t - \epsilon], \\ \mathrm{E}_y &= \mathrm{A} \sin 2\pi \mathrm{N}t \cos [2\pi(\nu + \mathrm{N})t - \epsilon], \end{aligned}\right\} \quad . \quad . \quad (6)$$

giving rise, therefore, to two circularly polarized waves of frequencies ν, $\nu + 2\mathrm{N}$. This is also readily interpreted in quantum theory, for just as in the inverse Zeeman effect here also circularly polarized light can cause absorption only in those transitions in which the absorbed angular momentum can be obtained directly from the angular momentum of the quanta constituting the light. In such a way it is found that

$$\left.\begin{aligned} &\nu_0 = \nu + \mathrm{N}, \\ \text{and} \quad &\nu' = \nu, \nu + 2\mathrm{N}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the sense of rotation of the incident light is the same as that of the model, both the classical and the quantum results are ν, $\nu - 2\mathrm{N}$.

The idea which we wish to put forward is that all frequency changes of the type described by (1) can be understood on a purely quantum basis either in a manner quite similar to that just described by (3), (4), (5), or by an alternative procedure to be described presently. The lack of generality in the above example is, of course, quite obvious. The oscillator in it executes a uniform motion of rotation, and its action depends very essentially on the polarization properties of the incident light. However, it embodies the main features of Righi's experiments. We think of each of the Nicol prisms in his apparatus as a collection of oscillators having all possible values of ν_0 in (3), (4), (5). Equation (4) determines which of these values concern us for a given ν, and the selection rule $\Delta n = \pm 1$ makes sure of the fact that the same ν_0 operates in re-emission.

2. *Righi's Experiment with Natural Light Incident on a Rotating Nicol.*

On this basis we can explain all of Righi's experiments with rotating nicols provided we understand correctly their meaning. Our reason for the extreme caution of the above statement is due to the fact that the most commonly known case of natural light passing through a rotating nicol does not lead directly to Righi's experimental result which we shall describe below. His result is due to a peculiar averaging out effect in the action of the quarter-wave plates and is connected only indirectly with equation (1).

We must recall here Righi's experimental arrangement. The light to be investigated falls in succession on a rotating Nicol prism, a pair of Fresnel mirrors, and a lens which forms a separate image of the reflexion from each mirror. Each image passes through a quarter-wave plate so oriented that the axes of the two plates are mutually perpendicular and form angles of 45° with the vertical. Both beams then traverse a double-image prism which separates the vertical vibrations from the horizontal ones. Two sets of moving fringes are observed through the double-image prism.

The usual explanation for the experiment with natural light is that the rotating nicol passes two circularly polarized beams, of frequencies $\nu \pm N$. The two circular components passing through one quarter-wave plate are resolved into a vertical disturbance with a frequency $\nu + N$ and a horizontal disturbance of frequency $\nu - N$. The light passing the other quarter-wave plate is resolved into vertical vibrations of frequency $\nu - N$ and horizontal ones of frequency $\nu + N$, since it is differently oriented.

It is very questionable, however, whether natural light on passing the first nicol may be said to give rise to the two circularly polarized beams. In fact, we may regard natural light as made up of a number of linearly polarized beams with random phases and random directions of polarization. If we do so, each linearly polarized ray on passing through the nicol gives rise to (*a*) a linearly polarized beam of frequency ν, and (*b*) two circularly polarized beams of frequencies $\nu \pm 2N$ as we have seen in (5). These three rays are coherent and the circular beams are of equal amplitude. Hence the analysis of natural light into linear vibrations leads to frequency changes $\nu, \nu \pm 2N$, rather than $\nu \pm N$ as is commonly supposed. Again, we may consider natural light as the result of superposition of a number of circularly polarized beams having random senses of polarization and

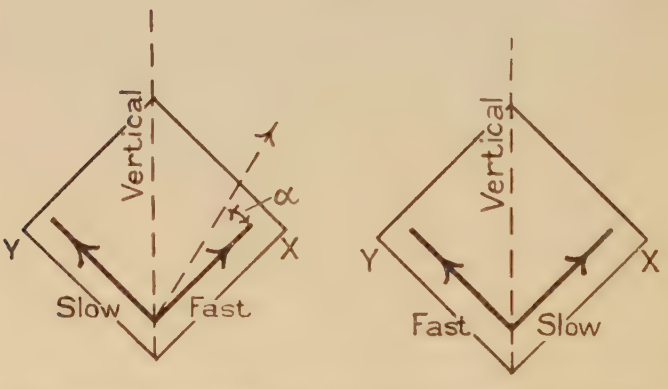
random phases. We have seen in (7) that such an analysis leads to a number of coherent trains of frequencies ν, $\nu+2N$, as well as to an equal number with frequencies ν, $\nu-2N$. In neither case, therefore, do we deal with frequencies $\nu\pm N$.

In spite of this it is possible to show that the random character of the phases of the components of the incident light leads to the production of an interference pattern, the fringes of which move with a velocity which corresponds exactly to that observed by Righi. The coherence of the trains ν, $\nu\pm2N$, is fundamental in this explanation as well as all others. We let

$$\omega=2\pi\nu, \quad \omega_0=2\pi N. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We suppose the incident light to be made up of linear beams.

Fig. 1.



The fast and slow axes in one of the quarter-wave plates are marked as X and Y and in the other as Y and X (see fig. 1). The direction of polarization of the incident beam is defined by the angle α in fig. 1. Equation (2) refers to a plane polarized wave with its electric vector along OX passing through a rotating nicol, having at time $t=0$ its short diagonal along OX. On passing through the nicol the wave appears as

$$E_x+iE_y=(1+e^{2i\omega_0 t})\cos(\omega t-\epsilon).$$

In this formula $\omega_0 t$ is the angle between the short diagonal of the nicol and the direction of polarization of the incident wave. In the general case, therefore, we must replace $\omega_0 t$ by $\omega_0 t-\alpha$, and further, we must multiply the result by

$e^{i\alpha}$ for the change of axes. In such a way we obtain for the electric intensity

$$X+iY=(e^{i\alpha}+e^{2i\omega_0 t-i\alpha})\cos(\omega t-\epsilon). \quad . \quad . \quad . \quad (9)$$

By means of (9) the vertical components of vibration transmitted by the two plates may be shown to be

$$\left.\begin{aligned} X'+Y' &= \cos(\omega t-\alpha-\epsilon)+\cos[(\omega-2\omega_0)t+\alpha-\epsilon], \\ X''+Y'' &= \sin[\omega(t-t_0)+\alpha-\epsilon] \\ &\quad +\sin[(\omega+2\omega_0)(t-t_0)-\alpha-\epsilon], \end{aligned}\right\} \quad (10)$$

where a relative retardation t_0 has been introduced. These expressions show what frequencies are present in the apparatus. On working out the intensity of the resulting interference pattern in a quasi-stationary manner, *i.e.*, supposing $\omega_0 << \omega$ and averaging over α the average intensity is found to be proportional to

$$I=1+\cos\omega_0 t_0 \sin[\omega_0(2t-t_0)-\omega t_0]. \quad . \quad . \quad (11)$$

If, on the other hand, two beams of frequencies $\nu \pm N$ are made to interfere, the resultant pattern is given by $1+\cos\{\omega_0(2t-t_0)-\omega t_0\}$. Our result (11) differs from this only on account of the presence of $\cos(\omega_0 t_0)$ and the unimportant phase $\frac{\pi}{2}$. Under all practical circumstances $\cos\omega_0 t_0 = 1$ because of the small value of $\omega_0 t_0$. Therefore, the general appearance of the pattern in Righi's apparatus must be identical with that due to two rays of frequencies $\nu \pm N$. However, the experiment is not by any means a demonstration of their existence. Quite on the contrary, *it is a proof of the coherence properties of rays of frequencies* ν, $\nu \pm 2N$

3. *Alternative Treatment of Frequency Change due to Modulation.*

The characteristic feature of the above treatment is that the rotating nicol is considered as a quantized system capable of absorption and re-emission. The nicol is thus thought of as unconnected with either the emitting or the absorbing atoms except by means of its absorption and emission. An alternative treatment is possible, however. We can try to look at the emitting atom and the rotating nicol as one complex generalized atom. The Correspondence Principle can then be applied directly to the generalized atom. For

example, the case of linearly polarized incident light described by equation (2) can be also represented, after proper phase change, as

$$E_x + iE_y = \frac{1}{4i}\left(e^{4\pi iNt} + 1\right)\left(e^{(2\pi\nu t-\epsilon)i} - e^{-(2\pi\nu t-\epsilon)i}\right). \quad (2')$$

The emitting atom may be taken to be for simplicity a linear oscillator. Then formula (3) applies provided n now is the quantum number of that oscillator. However, the selection rule becomes now

$$\Delta n = \pm 1, \quad \Delta j = 0, \pm 2,$$

as is seen from (2'). It is clear that the result given by (5) is correct also on this point of view, though the derivation is different. This is quite analogous to the relation of the Compton effect to the Doppler shift, for it is possible to think of the Compton effect either in one step, *i. e.*, by looking only at the initial and the final state of affairs, or else in two—first considering the absorption of a quantum by an electron and then its re-emission.

Our second point of view which we have just outlined has the advantage of being easy to generalize to practically all cases. Let us consider, for instance, a beam of light passing through a small hole and let the hole be covered by a rotating sectored disk or else by a rotating disk of varying opacity. If N is the number of revolutions of the disk per second, we can apply equation (1) by means of a proper choice of a_n. According to the Correspondence Principle, the probabilities of transitions in which the rotational quantum number j changes by $\pm n$ are connected with a_n^2. As long as the frequency changes nN are small compared with ν we may take the actual probabilities to be represented by a_n^2. Hence applying (3) we have an exact agreement both in intensities and frequencies between the classical and quantum theories as long as the approximations in (3) are justified. This, of course, is a consequence of Bohr's Correspondence Theorem for frequencies and involves only the fact that the contributions due to the rotating disk are for high quantum numbers, its frequency of rotation, and its overtones. We may be excused, therefore, from a further quantitative discussion of this matter provided we make clear the fundamental point, viz., that it is not necessary to think of light as made of vibrations in order to explain frequency changes due to variations in intensity. These may always be understood in terms of energy changes in the apparatus modifying

the transmission in general connexion with the formula

$$\frac{\delta W}{h} = \omega \frac{\delta J}{h} = (0, 1, 2, \dots)\omega,$$

where δW is the energy change of the transmitting apparatus, J is the momentum conjugate to the angular variable w of the system producing intensity changes, and $\omega = \frac{dw}{dt}$. [This system is supposed to have one degree of freedom, for simplicity.]

While in the case of a nicol it is possible to use either of the points of view proposed here, it seems very unreasonable to attach much significance to the first point of view [absorption and re-emission] in the case of a sectored disk.

4. *Coherence Relations and Applications to other Types of Observing Apparatus.*

The experimental evidence which we have used differs from that of the Compton effect on account of the importance which coherent wave-trains play in it. Righi's experiments, as we have shown above, prove that rays of different frequencies may be coherent. Similarly moving fringes in a Michelson interferometer which result when one of the mirrors is moved may be understood, as has been pointed out by A. B. Porter, in terms of light beats. They also demonstrate the preservation of phase which in this case applies to Schroedinger's Doppler effect mechanism. Similarly, if ordinary X-ray scattering is interpreted as the limiting case of the Compton scattering,—calculated for large values of the mass of the scattering entity, because of the tightness of binding between the electron and nucleus,—we have a demonstration of the preservation of phase in that case also. The case of the Compton effect itself is, of course, complicated by the varying recoil velocities of the electrons.

The present experimental evidence indicates, therefore, that such preservations of phase are universal. If it is correct to regard the scattering apparatus together with the emitting atom as one big atom, we have to conclude that *the various related lines emitted by an atom are also coherent* and that the only reason why we are not conscious of the fact is that their frequency differences are too large. Thus the Zeeman effect corresponding to 0·01 gauss would cause a frequency difference of the order of 10^5 a second, and hence no stationary pattern could be observed.

The above theory opens the possibility of quantum analogies of the action of various types of polarizing apparatus,

such as Nicol prisms, and quarter-wave and half-wave plates. It is only necessary to consider such polarizers as rotating oscillators which turn very slowly. Equation (3) shows that very small values of N may correspond to values of j which are large compared with unity.

The case of apparatus for producing elliptically polarized light is more complex. Here it is most convenient to adopt the method of treatment outlined in section 3. We might then suppose that the probabilities of emissions giving rise to circularly polarized light and those giving rise to linear light are exactly proportional to the squares of the corresponding amplitude coefficients, in spite of the fact that the angle of rotation may vary extremely slowly. Here also it is necessary to suppose that the coherence relations are those characteristic of the classical theory.

The methods of this paper also yield the ponderomotive effects of polarized light incident on material media, in agreement with the results of classical electrodynamics. The questions discussed in this paper are closely allied to a suggestion of Einstein * and its discussion by Joos †, dealing with frequency changes produced by modulation.

The above description of the action of polarizers is little more than a translation of the results of classical theory. However, the experimental facts concerning the Compton shift seem to make it worth while to see what results can be obtained from an extreme form of the quantum theory by making use of the conservation of angular momentum.

Washington, D.C.,
July 9, 1926.

CXXVII. *Chemical Valency.* *By* C. D. Niven, *B.Sc., M.A.*, *Research Student, University of Toronto* ‡.

I. *Introduction.*

THROUGH the recent advances made in spectroscopy, it is now possible to indicate how the extra nuclear electrons in the atoms of all the elements may be classified into groups representative of the types of orbits in which the electrons may be supposed to revolve or circulate.

Table I., which is taken from a paper by Professor McLennan and his collaborators, shows clearly the character of the orbits in which the electrons are supposed to revolve.

* *Naturwissenschaften*, xiv. p. 303 (1926).
† *Physik. Zs.* xxvii. p. 401 (1926).
‡ Communicated by Prof. J. C. McLennan, F.R.S.

TABLE I.

| Element. | Atomic Number. | Extra-nuclear Electronic Configurations. | | |

TABLE I. (*continued*).

Element.	Atomic Number.	Extra-nuclear Electronic Configurations.						
		K	L	M	N	O	P	Q
		1_1	2_1 2_2	3_1 3_2 3_3	4_1 4_2 4_3 4_4	5_1 5_2 5_3 5_4 5_5	6_1 6_2 6_3 6_4 6_5 6_6	7_1 7_2 7_3
In ...	49	2	2 6	2 6 10	2 6 10	2 1		
Sn ...	50	2	2 6	2 6 10	2 6 10	2 2		
Sb ...	51	2	2 6	2 6 10	2 6 10	2 3		
Te ...	52	2	2 6	2 6 10	2 6 10	2 4		
I ...	53	2	2 6	2 6 10	2 6 10	2 5		
Xe ...	54	2	2 6	2 6 10	2 6 10	2 6		
Cs ...	55	2	2 6	2 6 10	2 6 10	2 6	1	
Ba ...	56	2	2 6	2 6 10	2 6 10	2 6	2	
La ...	57	2	2 6	2 6 10	2 6 10	2 6 1	2	
Ce ...	58	2	2 6	2 6 10	2 6 10 1	2 6 1	2	
Pr ...	59	2	2 6	2 6 10	2 6 10 2	2 6 1	2	
Nd ...	60	2	2 6	2 6 10	2 6 10 3	2 6 1	2	
Ill ...	61	2	2 6	2 6 10	2 6 10 4	2 6 1	2	
Sa ...	62	2	2 6	2 6 10	2 6 10 5	2 6 1	2	
Eu ...	63	2	2 6	2 6 10	2 6 10 6	2 6 1	2	
Gd ...	64	2	2 6	2 6 10	2 6 10 7	2 6 1	2	
Tb ...	65	2	2 6	2 6 10	2 6 10 8	2 6 1	2	
Ds ...	66	2	2 6	2 6 10	2 6 10 9	2 6 1	2	
Ho ...	67	2	2 6	2 6 10	2 6 10 10	2 6 1	2	
Er ...	68	2	2 6	2 6 10	2 6 10 11	2 6 1	2	
Tu ...	69	2	2 6	2 6 10	2 6 10 12	2 6 1	2	
Yb ...	70	2	2 6	2 6 10	2 6 10 13	2 6 1	2	
Lu ...	71	2	2 6	2 6 10	2 6 10 14	2 6 1	2	
Hf ...	72	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
Ta ...	73	2	2 6	2 6 10	2 6 10 14	2 6 3	2	
W ...	74	2	2 6	2 6 10	2 6 10 14	2 6 4	2	
Rn ...	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
Os ...	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
Ir ...	77	2	2 6	2 6 10	2 6 10 14	2 6 7	2	
Pt ...	78	2	2 6	2 6 10	2 6 10 14	2 6 8	2	
Au ...	79	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
Hg ...	80	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
Tl ...	81	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
Pb ...	82	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2	
Bi ...	83	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
Po ...	84	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
EkaI.	85	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
Nt ...	86	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
EkaCs	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
Ra ...	88	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
Ac ...	89	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
Th ...	90	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2
Ux ...	91	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 3	2
Ur ...	92	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 4	2

The total quantum number "n," in so far as any one orbit is concerned, determines the major diameter of the elliptic orbit, while the azimuthal quantum number "k" determines

the angular momentum associated with an electronic orbit and also the minor axis of such an orbit.

According to this classification the maximum number of electrons describing orbits of total quantum number "n" and azimuthal quantum number "k" is $2(2k-1)$. Thus, for example, if $k=2$ there are at most six electrons in n_2 orbits, no matter what value be assigned to "n". As "k" has all integral values from 1 to n, the number of elements in a period should be $\sum_1^n 2(2k-1)$, which, if summed as an arithmetical progression series, is equal to Langmuir's expression $2n^2$.

It will be seen that in the development of atomic systems the electrons do not fill in the table quite regularly, especially where the higher elements are concerned. The first instance of such irregularities appears with the element potassium, where the nineteenth electron selects a 4_1 orbit in preference to a 3_3 one. Similar irregularities also occur with the elements rubidium and cæsium. It is this irregularity, however, in the binding of electrons to atomic nuclei that enables us to account for the existence of the two groups of atoms, scandium to nickel, and yttrium to palladium, as well as for the occurrence of the group of rare earths, lanthanum to lutecium. The classification of the elements as arranged by Bohr and as given in Table II. will make this point clear.

For the classification of radiations of the X-ray type that are emissible by atoms, it is necessary to expand the classification of orbits given in Table I. by subdividing the classes or groups according to the ideas of Main Smith and Stoner. As worked out by them, the electronic orbits in atoms are divided into the following classes :—

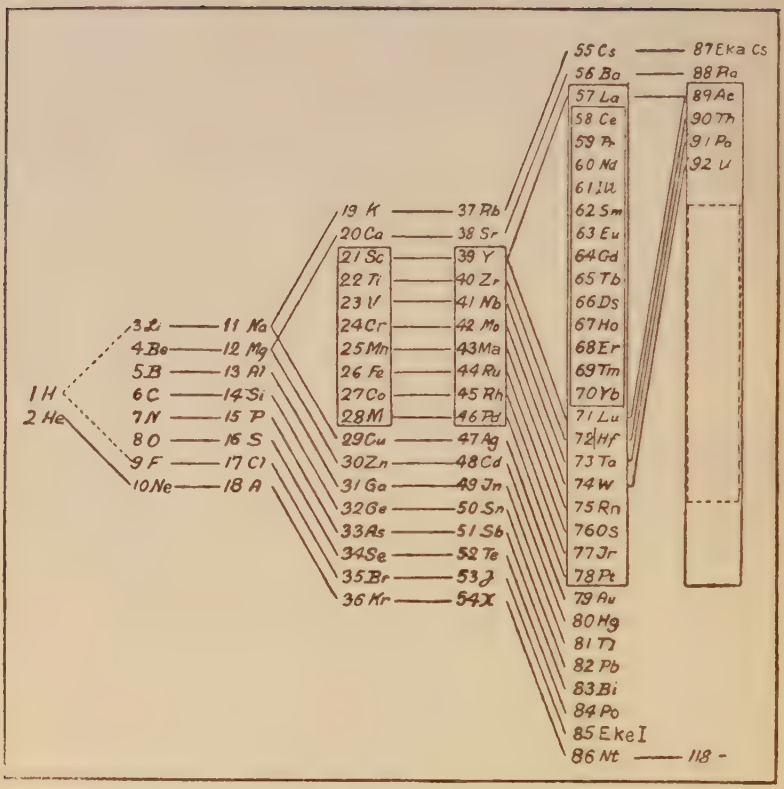
$$n_{kj}\ 1_{11},\ \ 2_{11}\ 2_{21},\ \ 3_{11}\ 3_{21}\ 3_{22}\ 3_{32}\ 3_{33},\ \ 4_{11}\ 4_{21}\ 4_{22}\ 4_{32}\ 4_{33}\ 4_{43}\ 4_{44},$$

etc., with a maximum number of electrons in an atom describing an orbit of the type n_{kj} being given by $2j$, where j is the so-called inner quantum number. Its numerical value is usually supposed to be a measure of the resultant angular momentum of the atom.

As the present communication is concerned wholly with a few of the outermost electronic orbits of each kind of atom, it will suffice for the purpose in view to confine oneself to a consideration of the arrangement of orbits given in Table I.

The connecting link between the results of spectroscopy as expressed in Table I. and their application to chemistry is found in the second part of Professor McLennan's Rule 10

TABLE II.



in his paper * on "Atomic States and Spectral Terms." "If an orbit type has a complete quota of electrons given by N (where $N=2(2k-1)$) and forms part of a given electron configuration of an atom, it can be neglected when deriving term types corresponding to that configuration." The basic assumption we shall therefore make is that a complete quota of electrons forms a stable system. The number of electrons to form a stable system is thus 2, 6, 10, 14. Hence, when compounds like sodium chloride are formed, the chlorine atom simply robs the sodium atom of its 3_1 electron to complete its own full quota—or "system"—of six 3_2 electrons. This process makes the chlorine atom negatively charged and the sodium atom positively charged, and they attract by the

* McLennan, Smith, and McLay, Proc. Roy. Soc. A, vol, cxii. p. 76 (1926).

electrostatic force to form sodium chloride. This polar bond has been known for some time, but the new classification of extra-nuclear electrons has given the conception tremendous power.

The rearrangement of electrons is obvious in simple combinations, such as halides, oxides, nitrides of metals ; electrons are simply robbed from the atoms of the metal to fill up the system of the electro-negative atom to its full number of six. Oxygen with its four electrons in its outermost system needs two more to complete that system, and therefore is not quite so reactive as a halide, while nitrogen requires three electrons to complete its system, and is less reactive still. Carbon has two electrons in its outside system, and therefore can take on four electrons to form carbides This system—complete only with six electrons in it and having only two of its places full—might be removed altogether, if the two electrons were removed by another atom to complete its own system. This happens in the case of carbon monoxide, where the oxygen atom acquires its full quota of electrons at the expense of the carbon atom. When, however, the carbon atom has been robbed of its two outermost electrons, the next two electrons, namely those in the 2_1 orbit, are exposed, and these also are robbed by another oxygen atom, with the result that carbon dioxide (CO_2) is formed. The two innermost electrons, *i. e.* in the 1_1 orbits, are in too stable equilibrium to be taken up by a third atom of oxygen.

2. *Diatomic Molecules.*

Before taking up the organic compounds, let us consider a few other elements, and in the first place those that are diatomic gases at normal temperature. For instance, consider hydrogen, which has one electron. If two atoms of hydrogen meet, one atom can rob the other of an electron and so form a completed system, as is well known, seeing that it only needs two 1_1 electrons to complete a system. This is why two hydrogen atoms can unite to form a diatomic molecule. It may be noted that the alkali metals form a very small percentage of molecules, although they also have a single electron in the outermost orbit. If these two electrons went to form a complete system, this system would have to be outside a ring of six electrons, generally, and apparently such a configuration is unstable.

The next element after hydrogen in the periodic system is helium, which, of course, does not combine with other elements, since its full quota of two electrons is present.

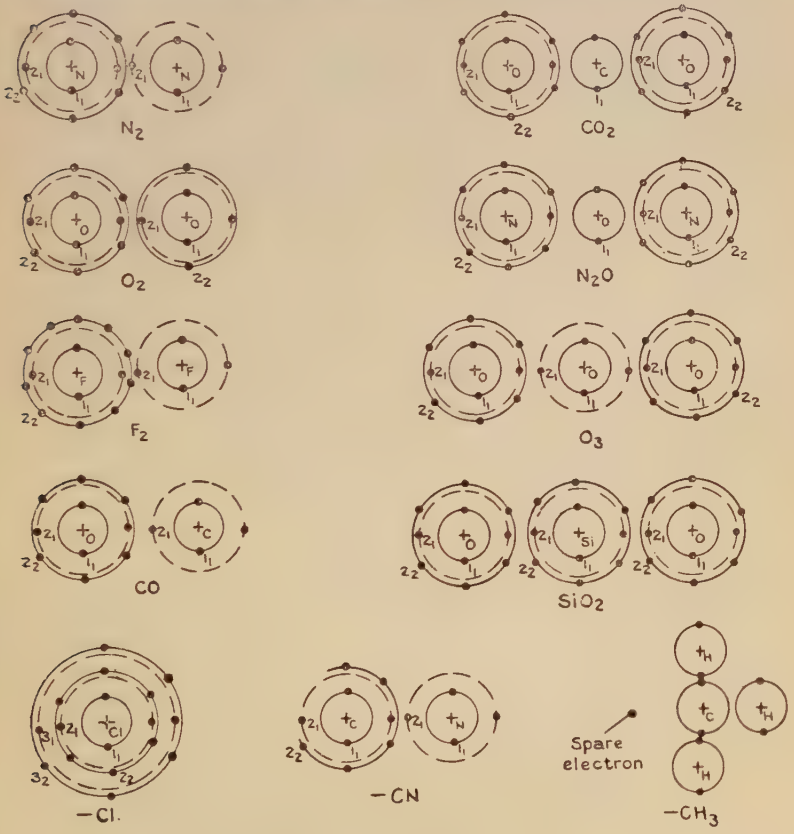
The next gaseous element after it is nitrogen. This gas forms diatomic molecules. The formation of these molecules is one of the most interesting confirmations of this theory. Nitrogen has three electrons of the type 2_2. Six 2_2 electrons are required to form a complete system, and hence, when two atoms unite, three electrons from each go to make the six electrons of the 2_2 system. These six electrons are exactly what are wanted to make stability, since every electron is in its right type of orbit. Nitrogen is therefore a very stable gas.

According, then, to the theory herein presented, nitrogen is not symmetrical. The same thing applies to all the diatomic elementary gases. This is possibly the reason why the crystal structures of these gases are so troublesome to determine. To assume that diatomic molecules are unsymmetrical, of course does not fit in with theories on band spectra which are based on a symmetrical molecule. A molecular structure which is symmetrical would mean that the centre of attraction of the moving electrons was at the centre of gravity of the two nuclei. So far as the mere grouping of the electrons from different combining atoms is concerned, it does not matter where the electrons of the resultant system are supposed to rotate. As the grouping is what determines the manner in which elements combine to form compounds, it will not affect the substance of this communication greatly whether the centre of attraction of the rotating electrons is one of the atomic nuclei or the centre of gravity of the two. W. L. Bragg * gives the atomic diameter for electronegative atoms of chromium and manganese as smaller than for electropositive atoms. This seems to indicate that the electrons are removed actually from one atom and given to another in combination. If such an interchange takes place in the formation of a salt, it is not unreasonable to suppose it takes place in other inorganic combinations. Hence, in making the diagram herewith, which shows a few illustrative examples of electronic configurations, the valence electrons are shown in rings round a particular nucleus : that nucleus is supposed to be their centre of attraction : the rings merely indicate systems, as of course the orbits have different orientations in space and are not necessarily circular.

In the oxygen atom there are four 2_2 electrons ; and when the molecule is formed there are eight electrons for the outside systems. Probably six go to form a complete system round one atom, and the remainder form a system

* W. L. Bragg, Phil. Mag. xl. p. 169 (1920).

of two 2_2 electrons. This would be a comparatively stable configuration, as two 2_2 electrons seem to be in stability in the case of carbon. Oxygen at normal temperatures is not very reactive if kept free from moisture except with very electropositive metals. The moisture, perhaps, has the effect of making this system of two 2_2 electrons unstable. Oxygen is much more easily dissociated than nitrogen because its structure is not nearly so stable.



Illustrative examples showing:—

(*a*) Similarity of CO_2 to N_2O, and of CO to N_2.

(*b*) Structures proposed for N_2, O_2, F_2, and O_3.

(*c*) Similarity of the atoms in SiO_2.

(*d*) Relation of $-CN$ to $-Cl$ and $-CH_3$.

In the case of fluorine, a very much more reactive gas is being dealt with. There are five 2_2 electrons in the fluorine

atom; and when two atoms unite to form a molecule, there is a system of ten formed instead of a system of six. This structure is not quite stable, as the inner system of six is not present. This explains the reactivity of fluorine and the halogens generally. Their configurations are all of the form ... : 2, 5, *i.e.* the last number is 5 and the second last 2. Therefore, when the molecule is formed, a system of ten is revolving around a system of two, without a system of six in between. It can easily be imagined that this would be unstable.

Serious objection might be raised to the stability of ten 2_2 electrons in a system, as it may be reasoned that if the electrons occupy 2_2 orbits there are only six possible types ; and if there are to be ten electrons in the system, either the electrons change to 3_3 orbits or two electrons occupy the same type of orbit. The first alternative assumes an increase in energy, while the second alternative violates Stoner's basic assumption that no two electrons can occupy the same type of orbit.

The fact remains, however, that there is an attraction between two fluorine atoms to form a molecule, and the formation of cyanogen gas (C_2N_2) adds additional evidence to the fact that some sort of bond exists between two systems, each of which has five spare electrons whose azimuthal quantum number is 2. It seems, therefore, that some sort of a system of ten is formed however serious the objections may be.

With regard to the second alternative, namely that two electrons of the same type occupy similar types of orbit, nothing much will be said : all theories of line spectra are based on the study of atoms in the free state ; in the molecule there are two nuclei. With regard to the first alternative—which assumes a change of energy—the formation of the chlorine molecule would not involve so much of an increase of energy ; the change would be from a 3_2 orbit to a 3_3 orbit, but this is large enough to show a line in the spectrum. Bromine would show less of a change still.

In connexion with elementary gases, mention might be made of ozone. Here one of the oxygen atoms is pictured as robbed of its four 2_2 electrons to make up the systems of the other two oxygen atoms to their full quota of six electrons.

3. *Oxides of Nitrogen.*

Let us now consider the compounds of nitrogen. Nitrogen has oxides N_2O_5, N_2O_3, N_2O_4, N_2O_2 (or NO), and N_2O, known

respectively as nitrogen pentoxide, nitrogen trioxide, nitric peroxide, nitric oxide, and nitrous oxide. In the compound nitrogen trioxide or nitrous anhydride (N_2O_3) each nitrogen atom is robbed of three electrons to fill up the outside system of the oxygen atom to the full quota of six. With the combination the 2_1 electrons of the nitrogen atoms are exposed and are available for other oxygen atoms; when these electrons are also robbed from the nitrogen atoms, nitrogen pentoxide is formed. In the case of nitric peroxide (N_2O_4) two of the oxygen atoms probably each rob a nitrogen atom of two electrons, and the other two oxygen atoms probably each take one of the remaining 2_2 nitrogen electrons apiece; the latter oxygen atoms are held together by the formation of an unstable system of ten electrons, as in the chlorine molecule. In the case of nitric oxide (N_2O_2) two nitrogen electrons go to form a system of two 2_2 electrons. Such a system was met with before in discussing oxygen, and seems to possess a little stability. In the case of both N_2O_2 and N_2O_4 the molecule can dissociate into NO and NO_2 with rise of temperature. This is because the two half molecules are held together by a bond which is not perfectly stable—in the one case two 2_2 electrons, and in the other case ten 2_2 electrons.

The last and lowest oxide of nitrogen, namely nitrous oxide (N_2O), can have its structure explained by this theory with great success, whilst the old valency theory demanded that oxygen be hexavalent. What happens, according to this theory, is that the four 2_2 electrons and the two 2_1 electrons are robbed from the oxygen atoms by the two nitrogen atoms making the outermost systems of the latter up to their full quota of six electrons; and therefore the electronic systems of carbon dioxide and nitrous oxide should be identical. The Lewis-Langmuir theory predicted a similarity between nitrous oxide and carbon dioxide, and between nitrogen and carbon monoxide, and this has been confirmed by work on crystal structure. The theory herein described indicates that the electronic configurations should be the same. This is confirmed by measurements on magnetic susceptibility in the case of carbon dioxide and nitrous oxide. Quinca finds that the volume magnetic susceptibilities of these two gases are equal at the same temperature and pressure.

It may be noted that the electronic structure of nitrous oxide differs from that of all of the other oxides of nitrogen in that nitrogen is acting as an electronegative element in nitrous oxide and electropositive in the other oxides. This

is quite in agreement with the experience of chemists ; a gradual change of properties is observed from the higher to the lower oxides of nitrogen until nitrous oxide is reached, but the properties of this gas do not fall into line with those of the others. Here seems to be a point in favour of the idea that the valence electrons are actually removed from one atom and given to another in combination ; for, if they were simply shared by the two atoms, there would be no sharp distinction between the nitrogen atom in nitrous oxide and the nitrogen atom in the other oxides.

The action of water on an oxide can clearly be seen, as, for instance, in the case of nitric acid. The oxygen atom in the middle of the nitric anhydride molecule does not have its system of electrons touched, but, instead of attracting the positively-charged cluster $-NO_2$, it exchanges it for a hydrogen proton, while the positively-charged $-NO_2$ group takes up the negatively-charged hydroxyl radicle, to form altogether a total of two molecules of nitric acid.

4. *Hydrides.*

The last compound of nitrogen we shall consider is ammonia. In this connexion it seems desirable to refer to the four hydrides—methane (CH_4), ammonia (NH_3), water (H_2O), and hydrofluoric acid (HF)—together. Two formulæ for ammonia could be proposed : firstly, the three hydrogen atoms could take up from the nitrogen atom a 2_2 electron apiece, to complete their own systems of 1_1 electrons ; or, secondly, the three hydrogen atoms could give up an electron each to complete the outermost system of the nitrogen atom. Almost the same remark could be made with regard to methane ; the carbon atom could take up four electrons from the four hydrogens and so complete its own system, or it could give up its two 2_2 and its two 2_1 electrons to complete the four hydrogen systems of two electrons. With oxygen, if two electrons were given up, two 2_2 electrons would be left on the oxygen atom ; or two hydrogen electrons could be taken on to make up the outer system of oxygen to six. With fluorine there is only one possibility, namely that the fluorine atom robs the hydrogen atom of its electron to complete its own outer system to six.

With fluorine, then, the arrangement is certain, but with oxygen, nitrogen, and carbon it is at first sight doubtful. Hydrofluoric acid is an acid hydride, forming fluorides readily. Water sometimes forms oxides ; ammonia rarely, if ever, forms nitrides ; and methane never forms carbides.

With these facts in mind, the isolated proton attached to the fluorine atom seems to suggest that what acidity really is, is the exposure of a proton—with no electrons around it. One can imagine the proton on the fluorine atom like the electron on a sodium atom. With methane and ammonia no acidity exists, and the arrangement whereby the hydrogen atoms have their systems of two 1_1 electrons filled at the expense of the carbon and nitrogen atoms will therefore be accepted as the right one. Water, however, presents a more difficult problem. Although water sometimes forms oxides, it seems very doubtful if it can be termed an acid. Water does not react acid with the usual acid indicators; and so it seems most likely that the protons are protected, and that the oxygen atom is left with a system of two 2_2 electrons. This would account for the little activity of water. Such a system was met with in nitric oxide and in the molecule of oxygen itself. This structure for oxygen leads to the conclusion that an hydroxide such as sodium hydroxide has the sodium atom bound to the oxygen atom with an unstable bond of two electrons.

If the structure of ammonia as given above be accepted, the ammonium salts can be easily explained. For, since the 2_1 electrons are exposed, a molecule of acid, such as hydrochloric acid, can take them both. The hydrogen atom takes one to complete its system of two electrons, and the chlorine atom takes the other to complete a system of six electrons. It is interesting to observe that in this way all four of the hydrogen atoms have their systems filled.

5. *Organic Compounds.*

So far, only inorganic compounds have been discussed; but, by a very small extension of the principle employed above, organic compounds can be explained as well. If the simplest aliphatic hydrocarbon, methane (CH_4), be considered, it seems probable that the two 2_2 electrons and the two 2_1 electrons are robbed by the hydrogen atoms to complete their 1_1 systems. If the next member, ethane, be taken, it seems probable that all the 2_2 electrons are robbed from the carbons and also one 2_1 electron from each carbon by the six hydrogen atoms, while the remaining 2_1 electrons form a closed system of two, as in the case of the hydrogen molecule, and in this way make a bond. If the third member of the paraffin series be considered, namely propane (C_3H_8), it may be seen that the first carbon atom of the chain, having three hydrogen atoms connected to it, supplies one

electron to form a bond with the second carbon atom. Two of the electrons are robbed from the second carbon atom by hydrogen atoms, a third one is used to form a system of two electrons with the electron from the first carbon of the chain, and the fourth to form a similar system with an electron from the third carbon of the chain. In this way as many carbon atoms as is pleased can be joined up in a chain. By assuming that the system of two moved round a carbon atom, it might be possible to explain the linking of two or even three carbon atoms in a chain by a mere electrostatic attraction; but when chains of four and more carbons are made up, such an explanation is impossible, because a carbon atom in the middle has an electron robbed by the carbon atom preceding it, and one given to it by the carbon atom coming after it in the chain. The total electrostatic effect must therefore be zero. This shows that this bond is not due to electrostatic attraction, and it seems reasonable to assume that it is due to a magnetic force. This possibly is why the organic compounds are so markedly different from the inorganic compounds.

The introduction of this two-electron system outside a group suggests at once the question that, if a two-electron system exists, can a six-electron system also exist in stability, since, in the study of inorganic compounds, a system of six electrons was very stable? The aromatic compounds answer this question in the affirmative. Benzene (C_6H_6), for instance, has the six carbons linked together in a ring by the two-electron bond, as explained for the chain compounds; and instead of having two hydrogen atoms bound to each carbon, there is only one, and the six spare electrons form a six-electron system somewhat like the outside system of a neon atom. In the same way hetero-cyclic rings are formed; all that is needed is that there be six spare electrons. The introduction of this conception supports the centric or Armstrong-Baeyer formula for benzene as opposed to Kekulé's formula, since it disposes of the fourth carbon bonds.

For a group of atoms, such as are found in organic compounds, to attach itself to a carbon atom in place of a hydrogen atom, all that is necessary with regard to its electronic configuration is that one more electron is required to complete its system. Instances of these groups are: $-OH$, $-NH_2$, $-COOH$, $-CHO$, and $-CN$. The $-OH$ group has already been dealt with in connexion with water. In the case of the $-NH_2$ group, the two hydrogen atoms rob the nitrogen atom of two of its three 2_2 electrons, and

the remaining 2_2 electron joins with the spare electron to form a system of two electrons similar to the special bond described above joining carbon atoms in a chain. The group $-COOH$ shows the carbon robbed of two electrons by the oxygen atom, and of a third by the $-OH$ group; the fourth electron joins with the spare electron to form the special carbon-to-carbon bond. In the case of the $-CHO$ group, the same thing occurs except that the hydrogen atom gets the electron taken by the hydroxyl part of the $-COOH$ group. With the cyanogen radicle, however, the usual inorganic bond is made. A cyanogen group is so much like a chlorine atom that their electronic configurations must have some point of resemblance. The characteristic of a chlorine atom is that it has an incompleted outer system of five electrons, thus requiring one electron to form a full quota. If, in the cyanogen radicle, the nitrogen atom robs the carbon atom of its two 2_2 electrons to make up its own 2_2 system to five, such a configuration has some resemblance to a chlorine atom ; or if the carbon robbed the nitrogen of its three 2_2 electrons, the same point of resemblance would exist. A cyanogen radicle, then, whether considered as $-CN$ or $-NC$, needs one electron to make up a system of six, and therefore it is only natural that it should resemble a halogen atom in its chemical behaviour.

The cyanogen radicle thus appears to differ from the other radicles in that it forms the usual inorganic bond, while the others all form the special two-electron bond. This suggests an explanation for using the $-CN$ radicle in synthesizing one carbon atom to another in building a chain. Before leaving the element carbon, it might be well to point out that carbon, on account of its power, as described above, to give up or take on four electrons, can have its tetrahedral crystal structure, as found in diamond, easily explained. Starting with one carbon atom, it can take on four electrons from four other carbon atoms becoming negatively charged ; these four other atoms each give up three electrons to other carbon atoms, and so on. In this way the different layers of atoms are alternately positive and negative, each atom inside the crystal being in perfect equilibrium electrostatically. To imagine two similar atoms positively and negatively charged in the same phase of a substance was at one time considered outlandish, but for the reasons considered in connexion with the nitrogen molecule, such a conception seems more than justified. When crystals are split, their cleavage faces frequently are positively and negatively charged, and this is a point in favour of the polar bond.

6. *Alternative Valencies.*

Ammonium chloride is an example of a compound in which nitrogen is pentavalent. Nitrogen becomes pentavalent when the two 2_1 electrons are taken as well as the 2_2 electrons. Oxygen is divalent so long as it is taking up electrons from other elements, and it seldom shows any other valency; on the other hand, sulphur, the next element in that group, shows the structure of group VI. admirably. Sulphur has two 3_1 and four 3_2 electrons; by picking up two hydrogen atoms it has its system of six 3_2 electrons filled. This happens in the case of sulphuretted hydrogen (H_2S). If it gives up the four 3_2 electrons to complete two oxygen systems of six 2_2 electrons, sulphur dioxide (SO_2) is formed. This exposes the two 3_1 electrons of the sulphur atom, and therefore sulphur trioxide (SO_3) can be formed by the third oxygen atom robbing the sulphur atom of these other two electrons.

With such structures as nitrogen and sulphur, alternative valency can be explained with ease: it occurs most frequently when the second outermost system gives up its electrons in addition to the outermost one. Hence the reason why two valencies differ by two so frequently for the same elements, *e. g.* nitrogen trivalent and pentavalent. Other interesting cases of the second outermost system giving up electrons are shown by manganese in potassium permanganate ($KMnO_4$) and chromium in potassium dichromate ($K_2Cr_2O_7$): in each of these compounds the 3_3 electrons are taken by oxygen atoms as well as the 4_1 electrons.

With elements like copper, palladium, and some others the spectroscopists have found that there are one or more other arrangements of the extra-nuclear electrons which correspond to "energy states" very little higher than the lowest. For instance, copper has its electrons arranged for a minimum of energy with ten electrons of the 3_3 type and one of the 4_1 type; but it is found that with nine electrons of the 3_3 type and two of the 4_1 type the energy of the system is increased by only a very small amount. The former arrangement gives the structure of copper in monovalent compounds, and the latter that in divalent compounds. Silver, which is always monovalent, is shown by spectroscopy to have only one possible structure for a low-energy level, namely ten electrons in the 4_3 system and one in the 5_1 system. Gold is usually monovalent and trivalent, and has two lowest energy levels, and from analogy with trivalent elements like aluminum it might be expected that if the one

arrangement would have ten 5_3 electrons and one 6_1 electron, the other arrangement would have eight 5_3 electrons, two 6_1 electrons, and one 6_2 electron; this does not appear to be so from the spectrum, and, indeed, such an arrangement on the Heisenberg-Hund theory corresponds to a fairly high-energy state. Spectroscopy indicates that gold should be divalent like copper. Again, with the element palladium the following oxides are found: Pd_2O, PdO, PdO_2. Three other structures should then be possible in addition to the one with ten electrons in the outermost ring, viz. (1) nine 4_3 and one 5_1 electrons; (2) eight 4_3 and two 5_1; and (3) six 4_3, two 5_1, and two 5_2. Both the first two structures are possible from spectroscopic considerations, but the last one is considered impossible as a low-energy state on the Heisenberg-Hund theory, and would break down at once.

It may be seen from these examples that there is a connexion between the alternative arrangements of electrons that give low-energy states and alternative chemical valencies—although chemical valencies appear which do not correspond to a low-energy state, as, for example, in trivalent gold. This must mean that the presence of the other atoms around the central atom is sufficient to change the conditions, so that one or more electrons become available as valence electrons, in addition to those in the outermost system. Such a change differs from that which occurs when sulphur, for instance, gives up its two 3_1 electrons and becomes hexavalent, since in that case a whole system of electrons becomes available as valence electrons.

Spectroscopic results are all based on the arrangement of the electrons when the atom is in free space, and therefore the fact that the presence of other atoms changes the arrangement is not by any means impossible. Again, in spectroscopy, when the electrons are arranged in one low-energy state, they cannot change to another low-energy state without first coming into a higher-energy state; in chemical reaction, experiment shows that the change can come about very easily, as, for instance, when a copper salt changes from a cuprous to a cupric salt; and therefore it is probable that the electrons do not need to come into a higher energy state.

To illustrate the connexion between alternative low-energy states and alternative valencies, Table III. has been constructed. This comprises some of the elements, showing in stable compounds valencies which cannot be explained by assuming—as in the case of sulphur—only one low-energy state. In the first column is given the element:

TABLE III.

Element.	Chemical Compound.	Extra-nuclear Electronic Configuration. K 1_1	L 2_1 2_2	M 3_1 3_2 3_3	N 4_1 4_2 4_3 4_4	O 5_1 5_2 5_3 5_4 5_5	P 6_1 6_2 6_3 6_4 6_5 6_6	Remarks.
Cr	—	2	2 6	2 6 5	1			Second outermo system whol removed in th
	$CrCl_2$	2	2 6	2 6 4	[2]			compounds CrC
	$CrCl_3$	2	2 6	2 6 3	[2 1]			and $K_2Cr_2O_7$.
Mn	MnO	2	2 6	2 6 5	[2]			Second outermo system whol removed in th
	Mn_2O_3	2	2 6	2 6 4	[2 1]			compound
	MnO_2	2	2 6	2 6 3	[2 2]			$KMnO_4$.
Fe	FeO	2	2 6	2 6 6	[2]			
	Fe_2O_3	2	2 6	2 6 5	[2 1]			
	FeS_2	2	2 6	2 6 4	[2 2]			
Co	$CoCl_2$	2	2 6	2 6 7	[2]			
	$CoCl_3$	2	2 6	2 6 6	[2 1]			
	CoS_2	2	2 6	2 6 5	[2 2]			
Ni	—	2	2 6	2 6 10				
	Ni_2S	2	2 6	2 6 9	[1]			
	NiO	2	2 6	2 6 8	[2]			
	Ni_2O_3	2	2 6	2 6 7	[2 1]			
	NiS_2	2	2 6	2 6 6	[2 2]			
Cu	Cu_2O	2	2 6	2 6 10	[1]			
	CuO	2	2 6	2 6 9	[2]			
Mo	—	2	2 6	2 6 10	2 6 5	1		Second outermo
	MoO	2	2 6	2 6 10	2 6 4	[2]		system whol
	Mo_2O_3	2	2 6	2 6 10	2 6 3	[2 1]		removed in th
	MoO_2	2	2 6	2 6 10	2 6 2	[2 2]		compounds Mo
	$MoCl_5$	2	2 6	2 6 10	2 6 1	[2 3]		and $Na_2Mo_2O_7$
Ru	—	2	2 6	2 6 10	2 6 7	1		Second outermo
	RuO	2	2 6	2 6 10	2 6 6	[2]		system whol
	Ru_2O_3	2	2 6	2 6 10	2 6 5	[2 1]		removed in th
	RuO_2	2	2 6	2 6 10	2 6 4	[2 2]		compound RuC
	K_2RuO_4	2	2 6	2 6 10	2 6 2	[2 4]		
	$KRuO_4$	2	2 6	2 6 10	2 6 1	[2 5]		
Rh	—	2	2 6	2 6 10	2 6 8	1		
	RhO	2	2 6	2 6 10	2 6 7	[2]		
	Rh_2O_3	2	2 6	2 6 10	2 6 6	[2 1]		
	RhO_2	2	2 6	2 6 10	2 6 5	[2 2]		
Pd	—	2	2 6	2 6 10	2 6 10			
	Pd_2O	2	2 6	2 6 10	2 6 9	[1]		
	PdO	2	2 6	2 6 10	2 6 8	[2]		
	PdO_2	2	2 6	2 6 10	2 6 6	[2 2]		

TABLE III. (*continued*).

Element.	Chemical Compound.	Extra-nuclear Electronic Configuration.						Remarks.
		K	L	M	N	O	P	
		1_1	2_1 2_2	3_1 3_2 3_3	4_1 4_2 4_3 4_4	5_1 5_2 5_3 5_4 5_5	6_1 6_2 6_3 6_4 6_5 6_6	
W	WCl_2	2	2 6	2 6 10	2 6 10 14	2 6 4	[2]	Second outermost system wholly removed in the compound WO_3.
	WCl_4	2	2 6	2 6 10	2 6 10 14	2 6 2	[2 2]	
	WCl_5	2	2 6	2 6 10	2 6 10 14	2 6 1	[2 3]	
Os	OsO	2	2 6	2 6 10	2 6 10 14	2 6 6	[2]	Second outermost system wholly removed in the compound OsO_4.
	Os_2O_3	2	2 6	2 6 10	2 6 10 14	2 6 5	[2 1]	
	OsO_2	2	2 6	2 6 10	2 6 10 14	2 6 4	[2 2]	
Ir	—	2	2 6	2 6 10	2 6 10 14	2 6 7	[2]	
	Ir_2O_3	2	2 6	2 6 10	2 6 10 14	2 6 6	[2 1]	
	IrO_2	2	2 6	2 6 10	2 6 10 14	2 6 5	[2 2]	
Pt	—	2	2 6	2 6 10	2 6 10 14	2 6 10		
	PtO	2	2 6	2 6 10	2 6 10 14	2 6 8	[2]	
	PtO_2	2	2 6	2 6 10	2 6 10 14	2 6 6	[2 2]	
Au	Au_2O	2	2 6	2 6 10	2 6 10 14	2 6 10	[1]	AuS is usually considered as auro-auric-sulphide Au_2S, Au_2S_3.
	AuS	2	2 6	2 6 10	2 6 10 14	2 6 9	[2]	
	$AuCl_3$	2	2 6	2 6 10	2 6 10 14	2 6 8	[2 1]	

in the second is given a compound typical of a certain valency; in the third is given the configuration of the extra-nuclear electrons, the numbers not in brackets referring to those electrons still on the atom, and the numbers in brackets referring to those robbed by the combining atoms. For purposes of comparison with the arrangement based on spectroscopy, these last are assigned to the different types of orbits which one would expect in simple atoms: for example, platinum in platinum tetrachloride, from analogy with carbon tetrachloride, has the valence electrons written (2, 2), and iron in ferric chloride has its three valence electrons written (2, 1), from analogy with aluminum trichloride. Neither of these arrangements is considered possible as a low-energy state from the spectroscopic standpoint.

When an element always occurs as a double atom in compounds in which it shows a particular valency, a corresponding electronic system is not given. The reason for omitting such a type is because the element may really have a higher valency than the compounds seem to show, and so

the extra-valency electrons may possibly be used to join the two atoms together as in the case of the carbon compounds. Thus in Hg_2Cl_2, mercury is probably divalent, though it appears monovalent.

A study of the table shows that, as a general rule, when the second outermost system of electrons in an atom is not full, combining atoms can rob it with great ease. Just as a system of two is unstable over a system of six, so a system of ten shows a little instability over a system of fourteen, as shown in platinum and gold. In the case of palladium * and silver, there is nothing larger than ten inside, and great stability is attained. The completing of these large systems for the first time seems to be difficult. The completion of the system of fourteen on the outside never occurs. This should show up in neodymium. The closing of a system of ten appears first in nickel, but a system of ten is not the normal state of nickel. Again, the fact that divalent copper predominates shows a similar instability of the system of ten. A system of six is too small, perhaps, to show any instability when first reached, but it would be expected from the above reasoning that sodium would show more tendency to be divalent than potassium would. Again, it may be observed that the elements preceding palladium and silver—namely molybdenum, ruthenium, and rhodium—show a remarkable variety of valencies. This is particularly interesting, as the system of ten is the stable configuration for palladium. It almost appears that, since the ideal configuration—namely ten electrons—is just missed, there is no decided preference for any other configuration. With nickel and platinum, as remarked above, the system of ten is not the ideal configuration, and the elements respectively preceding them show only three alternative configurations apiece. Another interesting inference from Table III. is that no element can give up more than eight electrons in forming a compound.

The elements in group III. of Mendeleeff's Table, such as aluminium, should show a monovalent character, just as carbon shows a divalent: but, as a matter of fact, this only appears in the heavier elements of this group. Thallium shows its monovalency character strongly: in fact, the monochloride is the stable chloride.

7. *Werner's Theory.*

Before concluding, reference must be made to Werner's coordination theory. Werner considered ammonium chloride (NH_4Cl) a coordination compound; but this type of

* McLennan and Smith, Proc. Roy. Soc., A, vol. cxii. (1926).

ammonium salt has been considered above, and successfully explained without reference to coordination numbers. Any attempt to explain double salts in a similar manner does not seem altogether successful. For instance, in the double salt K_4PtCl_6 it might be taken that four of the six 5_3 electrons, in the platinum atom, join with the two potassium atoms and the two chlorine atoms; but such a bond with the potassium atom seems improbable, and, furthermore, such an explanation is not possible in the case of potassium ferrocyanide (K_4FeCy_6). What seems more likely is that after the four chlorine electrons have removed the four outer electrons from the platinum atom, the incomplete system of six 5_3 electrons is exposed, and then an interchange of electrons takes place, whereby two 4_1 electrons from the two potassium atoms go into the platinum system and at the same time an equal number of electrons leave the platinum system to complete the chlorine systems, with the result that all the atoms get attracted to the platinum atom; the number of atoms that can be attracted in this way might be determined by the space they occupy, rather than by the number of electrons on the platinum atom, since for every electron added to the platinum atom one is subtracted. Possibly the reason for the so-called transition elements being so particularly apt to form these double salts is that an incomplete system is exposed ready to catch an electron after the valence electrons have been robbed. This electronic theory, therefore, does not seem at variance with Werner's coordination theory.

8. *Summary.*

The following is a summary of the foregoing paper dealing with the application of the Heisenberg-Hund model of the extra-nuclear electronic configurations in the atom to chemical compounds :—

1. It is concluded that diatomic elementary gases should have an unsymmetrical structure.
2. The chemical inertness of nitrogen is explained.
3. The difference between the properties of N_2O and the other oxides of nitrogen is explained.
4. Reasons are given for concluding that carbon dioxide and nitrous oxide should have the same electronic arrangements: thus an explanation is given for their similarity of crystal structure and magnetic properties.
5. Acidity, it is suggested, is due to exposed protons.
6. The distinction between the ordinary inorganic and

organic compounds is attributed to the ability of carbon atoms to form a sort of magnetic bond instead of an electrostatic one.

7. A reason is given for the stability of cyclic and heterocyclic rings in the aromatic compounds, which would justify the centric formula for benzene.

8. The similarity of the cyanogen radicle to a halogen atom is accounted for; its value in synthesis is explained.

9. An explanation of the structure of diamond is given without reference to a two-electron bond.

10. A discussion is given on the appearance of valencies other than that normally expected; these are traced to the second outermost system supplying valence electrons. Although the extra-nuclear electronic configurations corresponding to low-energy levels found spectroscopically usually show an alternative valency, it is shown that there are other valencies which would not be predicted from the spectrum of the element. A table is given showing different electronic configurations corresponding to different valencies, and deductions are made therefrom regarding the stability of different systems.

11. A short reference is made to Werner's Coordination Theory to connect the electronic theory of chemical combination with it.

In conclusion, I wish to express my gratitude to the National Research Council of Canada for grants of money that have enabled me to undertake research in Physics; also to Professor J. C. McLennan, F.R.S., whose inspiring lectures on atomic structure instigated this paper, for his assistance and advice; to Dr. Francis Gray, of Aberdeen, for his criticisms as a physical chemist; and to Dr. H. Grayson Smith for his help on several spectroscopic points.

CXXVIII. *Theory of a Polyphase Alternate Current Generator.* By W. C. Clinton *.

Summary.

The paper is an extension of T. R. Lyle's work on the simplest form of single phase alternator to the same form of multiphase machine. General expressions for the currents in any phase of such a machine are deduced in terms of the

* Communicated by the Author.

electrical constants of the circuits, the electromotive force in the exciting circuit, and the frequency. The conditions under which higher harmonics make their appearance in any of the circuits are examined, and the conditions to be fulfilled for their suppression are arrived at.

IN a little known but very valuable paper *, T. R. Lyle has worked out completely the theory of a single phase alternator reduced to its simplest elements of two air solenoids, one revolving inside the other. His results have since been obtained by others, the demonstration given by B. Liebowitz † of Pupin's method of determining the successive current harmonics that must necessarily appear in both circuits of such a machine when loaded, being the most convenient for use in the following extension of the theory to a polyphase machine of the same air-core type.

The structure of such a simplified polyphase machine and the conditions of operation under which it is to be investigated may be summarized thus :—

Each coil on the armature consists of a single turn in one plane, and all coils are exactly alike. Each coil is brought out to its own slip rings, or, alternatively, there may be $n+1$ rings to n coils, but arranged so that in either case each coil can be separately loaded. The coils rotate at a uniform angular speed ω on a common axis in their own planes and at right angles to the uniform field of the exciting solenoid, so that each coil in turn is penetrated by the maximum field flux, the penetration per ampere of excitation in any other position being given by $M\cos(\alpha+\phi_1)$ where $\alpha=\omega t$, and t is measured from the instant when for a given coil, say the first of the series, the penetration is $M\cos\phi_1$. M is the maximum value of mutual inductance between an armature coil and the solenoidal field winding.

Let N be the self-inductance of the field-winding, R the total resistance of its circuit, E the constant E.M.F. in it, and i the current at any time sufficiently long after closing the field switch for the transients to have died out.

* T. R. Lyle, "Theory of the Alternate Current Generator," Phil. Mag. 1909, vol. xviii. (ser. 6) p. 45, and 'Electrician,' vol. lxxi. pp. 1004–1007, Sept. 26, 1913.

† B. Liebowitz, "The Pupin Theory of Asymmetrical Rotors in Unidirectional Fields with special reference to the Goldschmidt Alternator," Proc. Inst. Radio Engineers, New York, vol. iii. p. 385, December 1915.

O. Lodge, Phil. Mag. vol. xxv. pp. 757–791, June 1913.

Let $L_1\ L_2\ L_3 \ldots L_n$ be the self-inductances of armature coils and circuits $1\ 2\ 3 \ldots n$ and $r_1\ r_2\ r_3 \ldots r_n$ be their resistances.

Let $M_{12}\ M_{23} \ldots M_{pq}$ be the mutual inductances between the different armature coils, M_{pq} being obviously the same as M_{qp}.

Let $\phi_1\ \phi_2\ \phi_3 \ldots \phi_n$ be the angular intervals of coils $1\ 2\ 3 \ldots n$ from an arbitrary datum, the angles being taken as positive in the direction of rotation.

The equation for the current in the field circuit is

$$N\frac{di}{dt} + \frac{dMi_1\cos(\alpha+\phi_1)}{dt} + \frac{dMi_2\cos(\alpha+\phi_2)}{dt} + \frac{dMi_3\cos(\alpha+\phi_3)}{dt} \ldots + \frac{dMi_n\cos(\alpha+\phi_n)}{dt} + Ri = E,$$

or

$$N\frac{di}{dt} + M\left(\frac{di_1\cos(\alpha+\phi_1)}{dt} + \frac{di_2\cos(\alpha+\phi_2)}{dt} + \frac{di_3\cos(\alpha+\phi_3)}{dt} \ldots + \frac{di_n\cos(\alpha+\phi_n)}{dt}\right) + Ri = E;$$

the equations for the currents in the several armature coils are:—

$$L_1\frac{di_1}{dt} + M\frac{di\cos(\alpha+\phi_1)}{dt} + M_{12}\frac{di_2}{dt} + M_{13}\frac{di_3}{dt} + \ldots M_{1n}\frac{di_n}{dt} + r_1i_1 = 0,$$

$$L_2\frac{di_2}{dt} + M\frac{di\cos(\alpha+\phi_2)}{dt} + M_{21}\frac{di_1}{dt} + M_{23}\frac{di_3}{dt} + \ldots M_{2n}\frac{di_n}{dt} + r_2i_2 = 0,$$

$$L_3\frac{di_3}{dt} + M\frac{di\cos(\alpha+\phi_2)}{dt} + M_{31}\frac{di_1}{dt} + M_{32}\frac{di_2}{dt} + \ldots M_{3n}\frac{di_n}{dt} + r_3i_3 = 0,$$

. . . . . .

$$L_n\frac{di_n}{dt} + M\frac{di\cos(\alpha+\phi_n)}{dt} + M_{n1}\frac{di_1}{dt} + M_{n2}\frac{di_2}{dt} \ldots M_{(n-1)n}\frac{di_{n-1}}{dt} + r_ni_n = 0.$$

Rewrite these equations so as to bring similar differentials vertically under one another on the left-hand side, remembering that inversion of suffixes of coefficients of mutual induction does not alter the value of the coefficient.

$$L_1\frac{di_1}{dt}+M_{12}\frac{di_2}{dt}+M_{13}\frac{di_3}{dt}+\ldots+M_{1n}\frac{di_n}{dt}+r_1i_1 = -M\frac{di\cos(\alpha+\phi_1)}{dt},$$

$$M_{12}\frac{di_1}{dt}+L_2\frac{di_2}{dt}+M_{23}\frac{di_3}{dt}+\ldots+M_{2n}\frac{di_n}{dt}+r_2i_2 = -M\frac{di\cos(\alpha+\phi_2)}{dt}$$

$$M_{13}\frac{di_1}{dt}+M_{23}\frac{di_2}{dt}+L_3\frac{di_3}{dt}+\ldots+M_{3n}\frac{di_n}{dt}+r_3i_3 = -M\frac{di\cos(\alpha+\phi_3)}{dt},$$

. . . . . .

$$M_{1n}\frac{di_1}{dt}+M_{2n}\frac{di_2}{dt}+M_{3n}\frac{di_3}{dt}+\ldots+L_n\frac{di_n}{dt}+r_ni_n = -M\frac{di\cos(\alpha+\phi_n)}{dt}.$$

Following the modified form of Lyle's solution for the single phase alternator as given by Pupin, the first constituent of the field current will be $\frac{E}{R}$. The remaining constituents of this current, and all the constituents of the armature currents, will be derived by writing differential equations to zero each only involving one frequency.

Thus there are n equations for the determination of n first harmonics of $i_1\ i_2\ i_3\ \ldots\ i_n$ of which the left-hand sides are as given above, and the right-hand sides are respectively:

$$\frac{ME\omega\sin(\alpha+\phi_1)}{R},\quad \frac{ME\omega\sin(\alpha+\phi_2)}{R},$$

$$\frac{ME\omega\sin(\alpha+\phi_3)}{R}\ldots\frac{ME\omega\sin(\alpha+\phi_n)}{R}.$$

Expressing the first harmonics of $i_1\ i_2\ i_3 \ldots i_n$ as

$$I_1 \sin(\alpha+\phi_1\pm\theta_1),\ I_2 \sin(\alpha+\phi_2\pm\theta_2),\ \ldots I_n \sin(\alpha+\phi_n\pm\theta_n),$$

each equation can then be taken as an identity in $\sin\alpha$ and $\cos\alpha$. There are thus $2n$ equations for the determination of the $2n$ unknown quantities,

$$I_1 \cos(\phi_1\pm\theta_1),\ I_2 \cos(\phi_2\pm\theta_2),\ \ldots I_n \cos(\phi_n\pm\theta_n),$$

$$I_1 \sin(\phi_1\pm\theta_1),\ I_2 \sin(\phi_2\pm\theta_2),\ \ldots I_n \sin(\phi_n\pm\theta_n).$$

If these are written

$$x_1, x_2, \ldots x_n,$$

$$y_1, y_2, \ldots y_n\ ;$$

if self-inductive reactances are written

$$L_1\omega = X_1,\ L_2\omega = X_2,\ L_n\omega = X_n,$$

and if mutual reactances are written

$$M_{12}\omega = Y_{12},\ M_{23}\omega = Y_{23},\ \ldots,$$

the $2n$ equations become :—

$$X_1x_1 + Y_{12}x_2 + Y_{13}x_3 + \ldots + Y_{1n}x_n - r_1y_1 = \frac{ME\omega}{R}\sin\phi_1,$$

$$X_1y_1 + Y_{12}y_2 + Y_{13}y_3 + \ldots + Y_{1n}y_n + r_1x_1 = \frac{ME\omega}{R}\cos\phi_1,$$

$$Y_{12}x_1 + X_2x_2 + Y_{23}x_3 + \ldots + Y_{2n}x_n - r_2y_2 = \frac{ME\omega}{R}\sin\phi_2,$$

$$Y_{12}y_1 + X_2y_2 + Y_{23}y_3 + \ldots + Y_{2n}y_n + r_2x_2 = \frac{ME\omega}{R}\cos\phi_2,$$

$$Y_{13}x_1 + Y_{23}x_2 + X_3x_3 + \ldots + Y_{3n}x_n - r_3y_3 = \frac{ME\omega}{R}\sin\phi_3,$$

$$Y_{13}y_1 + Y_{23}y_2 + X_3y_3 + \ldots + Y_{3n}y_n + r_3x_3 = \frac{ME\omega}{R}\cos\phi_3,$$

. . . . . .

$$Y_{1n}x_1 + Y_{2n}x_2 + Y_{3n}x_3 + \ldots + X_nx_n - r_ny_n = \frac{ME\omega}{R}\sin\phi_n,$$

$$Y_{1n}y_1 + Y_{2n}y_2 + Y_{3n}y_3 + \ldots + X_ny_n - r_nx_n = \frac{ME\omega}{R}\cos\phi_n.$$

Re-arranging so as to be convenient for determinant solution by grouping together the sine and cosine equations and supplying the terms with zero coefficients where necessary, there results :—

$$X_1x_1 + Y_{12}x_2 + Y_{13}x_3 + \ldots + Y_{1n}x_n - r_1y_1 + 0y_2 + 0y_3 + \ldots + 0y_n = \frac{ME\omega}{R}\sin\phi_1,$$

$$Y_{12}x_1 + X_2x_2 + Y_{23}x_3 + \ldots + Y_{2n}x_n + 0y_1 - r_2y_2 + 0y_3 + \ldots + 0y_n = \frac{ME\omega}{R}\sin\phi_2,$$

$$Y_{13}x_1 + Y_{23}x_2 + X_3x_3 + \ldots + Y_{3n}x_n + 0y_1 + 0y_2 - r_3y_3 + \ldots + 0y_n = \frac{ME\omega}{R}\sin\phi_3,$$

. . . . . .

$$Y_{1n}x_1 + Y_{2n}x_2 + Y_{3n}x_3 + \ldots + X_nx_n + 0y_1 + 0y_2 + 0y_3 + \ldots - r_ny_n = \frac{ME\omega}{R}\sin\phi_n,$$

$$r_1x_1 + 0x_2 + 0x_3 + \ldots + 0x_n + X_1y_1 + Y_{12}y_2 + Y_{13}y_3 + \ldots + Y_{1n}y_n = \frac{ME\omega}{R}\cos\phi_1,$$

$$0x_1 + r_2x_2 + 0x_3 + \ldots + 0x_n + Y_{12}y_1 + X_2y_2 + Y_{23}y_3 + \ldots + Y_{2n}y_n = \frac{ME\omega}{R}\cos\phi_2,$$

$$0x_1 + 0x_2 + r_3x_3 + \ldots + 0x_n + Y_{13}y_1 + Y_{23}y_2 + X_3y_3 + \ldots + Y_{3n}y_n = \frac{ME\omega}{R}\cos\phi_3,$$

. . . . . .

$$0x_1 + 0x_2 + 0x_3 + \ldots + r_nx_n + Y_{1n}y_1 + Y_{2n}y_2 + Y_{n3}y_3 + \ldots + X_ny_n = \frac{ME\omega}{R}\cos\phi_n.$$

The values of $x_1\,x_2\,x_3\,\ldots\,x_n$, $y_1\,y_2\,y_3\,\ldots\,y_n$ can be written down as the ratio of two determinants of which the denomi-

nator determinant is the same for all and equal to

$$\begin{vmatrix}
X_1 & Y_{12} & Y_{13} & \dots & Y_{1n} & -r_1 & 0 & 0 & 0 & \dots & 0 \\
Y_{12} & X_2 & Y_{23} & \dots & Y_{2n} & 0 & -r_2 & 0 & 0 & \dots & 0 \\
Y_{13} & Y_{23} & X_3 & \dots & Y_{3n} & 0 & 0 & -r_3 & 0 & \dots & 0 \\
 & & & & & & & & & & \\
Y_{1n} & Y_{2n} & Y_{3n} & \dots & X_n & 0 & 0 & 0 & & \dots & -r_n \\
r_1 & 0 & 0 & \dots & 0 & X_1 & Y_{12} & Y_{13} & & \dots & Y_{1n} \\
0 & r_2 & 0 & \dots & 0 & Y_{12} & X_2 & Y_{23} & & \dots & Y_{2n} \\
0 & 0 & r_3 & \dots & 0 & Y_{13} & Y_{23} & X_3 & & \dots & Y_{3n} \\
 & & & & & & & & & & \\
0 & 0 & 0 & \dots & r_n & Y_{1n} & Y_{2n} & Y_{3n} & & \dots & X_n
\end{vmatrix}$$

As I_1 is $\sqrt{x_1^2 + y_1^2}$, the numerator for I_1 is

$$\frac{EM\omega}{R}\left\{\begin{vmatrix}
\sin\phi_1 & Y_{12} & Y_{13} & \dots & Y_{1n} & -r_1 & 0 & 0 & \dots & 0 \\
\sin\phi_2 & X_2 & Y_{23} & \dots & Y_{2n} & 0 & -r_2 & 0 & \dots & 0 \\
\sin\phi_3 & Y_{23} & X_3 & \dots & Y_{3n} & 0 & 0 & -r_3 & \dots & 0 \\
 & & & & & & & & & \\
\sin\phi_n & Y_{2n} & Y_{3n} & \dots & X_n & 0 & 0 & 0 & \dots & r_n \\
\cos\phi_1 & 0 & 0 & \dots & 0 & X_1 & Y_{12} & Y_{13} & \dots & Y_{1n} \\
\cos\phi_2 & r_2 & 0 & \dots & 0 & Y_{12} & X_2 & Y_{23} & \dots & Y_{2n} \\
\cos\phi_3 & 0 & r_3 & \dots & 0 & Y_{13} & Y_{23} & X_3 & \dots & Y_{3n} \\
 & & & & & & & & & \\
\cos\phi_n & 0 & 0 & \dots & r_n & Y_{1n} & Y_{2n} & Y_{3n} & \dots & X_n
\end{vmatrix}^2\right.$$

$$+\left\{\begin{vmatrix}
X_1 & Y_{12} & Y_{13} & \dots & Y_{1n} & \sin\phi_1 & 0 & 0 & \dots & 0 \\
Y_{12} & X_2 & Y_{23} & \dots & Y_{2n} & \sin\phi_2 & -r_2 & 0 & \dots & 0 \\
Y_{13} & Y_{23} & X_3 & \dots & Y_{3n} & \sin\phi_3 & 0 & -r_3 & \dots & 0 \\
 & & & & & & & & & \\
Y_{1n} & Y_{2n} & Y_{3n} & \dots & X_n & \sin\phi_n & 0 & 0 & \dots & -r_n \\
r_1 & 0 & 0 & \dots & 0 & \cos\phi_1 & Y_{12} & Y_{13} & \dots & Y_{1n} \\
0 & r_2 & 0 & \dots & 0 & \cos\phi_2 & X_2 & Y_{23} & \dots & Y_{2n} \\
0 & 0 & r_3 & \dots & 0 & \cos\phi_3 & Y_{23} & X_3 & \dots & Y_{3n} \\
 & & & & & & & & & \\
0 & 0 & 0 & \dots & r_n & \cos\phi_n & Y_{2n} & Y_{3n} & \dots & X_n
\end{vmatrix}^2\right\}$$

and the tangent of the angle of phase difference between I_1 and the arbitrary datum is given by the ratio of the two determinants :

$$\begin{vmatrix}
X_1 & Y_{12} & Y_{13} & \dots & Y_{1n} & \sin\phi_1 & 0 & 0 & \dots & 0 \\
Y_{12} & X_2 & Y_{23} & \dots & Y_{2n} & \sin\phi_2 & -r_2 & 0 & \dots & 0 \\
Y_{13} & Y_{23} & X_3 & \dots & Y_{3n} & \sin\phi_3 & 0 & -r_3 & \dots & 0 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
Y_{1n} & Y_{2n} & Y_{3n} & \dots & X_n & \sin\phi_n & 0 & 0 & \dots & -r_n \\
r_1 & 0 & 0 & \dots & 0 & \cos\phi_1 & Y_{12} & Y_{13} & \dots & Y_{1n} \\
0 & r_2 & 0 & \dots & 0 & \cos\phi_2 & X_2 & Y_{23} & \dots & Y_{2n} \\
0 & 0 & r_3 & \dots & 0 & \cos\phi_3 & Y_{23} & X_3 & \dots & Y_{3n} \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
0 & 0 & 0 & \dots & r_n & \cos\phi_n & Y_{2n} & Y_{3n} & \dots & X_n
\end{vmatrix}$$

$$\begin{vmatrix}
\sin\phi_1 & Y_{12} & Y_{13} & \dots & Y_{1n} & -r_1 & 0 & 0 & \dots & 0 \\
\sin\phi_2 & X_2 & Y_{23} & \dots & Y_{2n} & 0 & -r_2 & 0 & \dots & 0 \\
\sin\phi_3 & Y_{23} & X_3 & \dots & Y_{3n} & 0 & 0 & -r_3 & \dots & 0 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\sin\phi_n & Y_{2n} & Y_{3n} & \dots & X_n & 0 & 0 & 0 & \dots & -r_n \\
\cos\phi_1 & 0 & 0 & \dots & 0 & X_1 & Y_{12} & Y_{13} & \dots & Y_{1n} \\
\cos\phi_2 & r_2 & 0 & \dots & 0 & Y_{12} & X_2 & Y_{23} & \dots & Y_{2n} \\
\cos\phi_3 & 0 & r_3 & \dots & 0 & Y_{13} & Y_{23} & X_3 & \dots & Y_{3n} \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cos\phi_n & 0 & 0 & \dots & r_n & Y_{1n} & Y_{2n} & Y_{3n} & \dots & X_n
\end{vmatrix}.$$

The numerators of $I_2 \dots I_n$, and the tangents of $(\phi_2 - \theta_2) \dots (\phi_n - \theta_n)$ can be obtained by moving the column $\sin\phi_1 \dots \cos\phi_n$ into the appropriate position in each of the two determinant expressions.

Thus the manner in which the constants of all the circuits influence the magnitude and relative phase of the first harmonic current in any one circuit is demonstrated. As the coefficients of mutual induction occur symmetrically, and as there are a number of zero constituents, these determinants are not quite so cumbersome as they look. Each of

them can be expanded into $2n!/(n!)^2$ nth minors and the subsequent reduction can be done systematically by well-known methods.

Thus if $n=2$,

$$I_1=\frac{EM\omega}{R}\sqrt{\frac{\begin{vmatrix}\sin\phi_1 & Y_{12} & -r_1 & 0\\ \sin\phi_2 & X_2 & 0 & -r_2\\ \cos\phi_1 & 0 & X_1 & Y_{12}\\ \cos\phi_2 & r_2 & Y_{12} & X_2\end{vmatrix}^2+\begin{vmatrix}X_1 & Y_{12} & \sin\phi_1 & 0\\ Y_{12} & X_2 & \sin\phi_2 & -r_2\\ r_1 & 0 & \cos\phi_1 & Y_{12}\\ 0 & r_2 & \cos\phi_2 & X_2\end{vmatrix}^2}{\begin{vmatrix}X_1 & Y_{12} & -r_1 & 0\\ Y_{12} & X_2 & 0 & -r_2\\ r_1 & 0 & X_1 & Y_{12}\\ 0 & r_2 & Y_{12} & X_2\end{vmatrix}}}$$

and

$$I_2=\frac{EM\omega}{R}\sqrt{\frac{\begin{vmatrix}X_1 & \sin\phi_1 & -r_1 & 0\\ Y_{12} & \sin\phi_2 & 0 & -r_2\\ r_1 & \cos\phi_1 & X_1 & Y_{12}\\ 0 & \cos\phi_2 & Y_{12} & X_2\end{vmatrix}^2+\begin{vmatrix}X_1 & Y_{12} & -r_1 & \sin\phi_1\\ Y_{12} & X_2 & 0 & \sin\phi_2\\ r_1 & 0 & X_1 & \cos\phi_1\\ 0 & r_2 & Y_{12} & \cos\phi_2\end{vmatrix}^2}{\begin{vmatrix}X_1 & Y_{12} & -r_1 & 0\\ Y_{12} & X_2 & 0 & -r_2\\ r_1 & 0 & X_1 & Y_{12}\\ 0 & r_2 & Y_{12} & X_2\end{vmatrix}}}$$

If it be assumed as a particular case that $r_1=r_2=r$, $X_1=X_2$, $\phi_1=0$ and $\phi_2=\frac{\pi}{2}$, then $Y_{12}=0$ and the above expressions easily give the well-known relations,

$$I_1=I_2=\frac{EM\omega}{R}\cdot\frac{1}{\sqrt{X^2+r^2}} \quad \text{and} \quad \tan\pm\theta_1=\frac{X}{r},$$

the angle of lag of I_2 from zero datum being $\frac{\pi}{2}\pm\theta_1$.

The coefficients of mutual and self induction can be calculated from the relative angular positions and dimensions of simple rectangular and circular coils, so that it would be possible in the case of such a simple multiphase alternator to state the armature currents in terms of exciting voltage, frequency, coil dimensions, and circuit resistances.

If these values of the first harmonic currents be substituted in the expression for the field current on p. 1336 the latter may be written

$$N\frac{di}{dt} + M\frac{d}{dt}\{I_1 \sin(\alpha+\phi_1\pm\theta_1)\cos(\alpha+\phi_1) + I_2 \sin(\alpha+\phi_2\pm\theta_2)\cos(\alpha+\phi_2) + \ldots + I_n \sin(\alpha+\phi_n\pm\theta_n)\cos(\alpha+\phi_n)\} + Ri = E,$$

performing the differentiation :

$$N\frac{di}{dt} + M\omega\{I_1\cos(2\alpha+2\phi_1\pm\theta_1) + I_2\cos(2\alpha+2\phi_2\pm\theta_2) + \ldots + I_n\cos(2\alpha+2\phi\pm\theta)\} + Ri = E.$$

If the expression within the main bracket be made zero by any arrangement whatever among the coefficients, then for that particular arrangement there would be no second harmonic in the field current, and no further harmonics than the first in any of the armature currents.

Assuming that all the circuits are loaded in any manner, $I_1 \ldots I_n$ can have any finite positive values, and $(\phi_1 \ldots \phi_n)$ can be any series of angular intervals from the arbitrary datum. The multiplier of $M\omega$ can be written :

$$\cos 2\alpha\{I_1\cos(2\phi_1\pm\theta_1) + I_2\cos(2\phi_2\pm\theta_2) + \ldots + I_n\cos(2\phi_n\pm\theta_n)\} -$$
$$\sin 2\alpha\{I_1\sin(2\phi_1\pm\theta_1) + I_2\sin(2\phi_2\pm\theta_2) + \ldots + I_n\sin(2\phi_n\pm\theta_n)\},$$

which is of the form

$$A\cos 2\alpha - B\sin 2\alpha = \sqrt{A^2+B^2}\cos(2\alpha+\sigma),$$

where $\tan\sigma = \frac{B}{A}$, B and A having, in general, finite positive values. Hence, if the multiplier is to be zero for all values of 2α, then $\sqrt{A^2+B^2}$ must be zero. That is,

$$I_1^2 + I_2^2 + \ldots + I_n^2 + \Sigma 2 I_1 I_2 \cos(2\phi_1\pm\theta_1)\cos(2\phi_2\pm\theta_2) + \Sigma 2 I_1 I_2 \sin(2\phi_1\pm\theta_1)\sin(2\phi_2\pm\theta_2)$$

must be zero, or

$$I_1^2 + I_2^2 + \ldots + I_n^2 + \Sigma 2 I_1 I_2 \cos(2\phi_1\pm\theta_1 - 2\phi_2\mp\theta_2) = 0,$$

where the number of terms under the sign of summation is $\frac{n(n-1)}{2}$ and the number of terms outside that sign is n.

Let $n=2$. The expression is then

$$I_1^2+I_2^2+2I_1I_2\cos(2\phi_1-2\phi_2\pm(\theta_1-\theta_2)=0,$$

and the condition is

$$\cos(2\phi_1-2\phi_2\pm(\theta_1-\theta_2))=-\frac{I_1^2+I_2^2}{2I_1I_2}.$$

The value of the right-hand expression is -1, when $I_1=I_2$, and the condition then becomes

$$\cos(2\phi_1-2\phi_2\pm(\theta_1-\theta_2))=1,$$

or
$$2\phi_1-2\phi_2\pm(\theta_1-\theta_2)=\pi.$$

For equally loaded circuits, $\theta_1=\theta_2$, and the phase difference of the position of the coils is then $\frac{\pi}{2}$.

That is, in the simplest type of two phase alternator, having both its circuits equally loaded, the phase angle between the coils on the alternator must be $\frac{\pi}{2}$ if there are to be no harmonics in the field circuit, and only the fundamental present in the armature circuits.

Let $n=3$. The expression is then

$$\begin{aligned}I_1^2+I_2^2+I_3^2+2\,I_1I_2\cos(2\phi_1-2\phi_2\pm(\theta_1-\theta_2))\\+2\,I_3I_1\cos(2\phi_3-2\phi_1\pm(\theta_3-\theta_1))\\+2\,I_2I_3\cos(2\phi_2-2\phi_3\pm(\theta_2-\theta_3))=0.\end{aligned}$$

Put

$$\phi_1-\phi_2=\psi_1 \text{ and } \phi_2-\phi_3=\psi_2, \quad \text{then} \quad \phi_1-\phi_3=\psi_1+\psi_2.$$

If the loading of the three circuits are similar, the criterion for the absence of harmonics becomes

$$3+2\cos 2\psi_1+2\cos 2\psi_2+2\cos 2(\psi_1+\psi_2)=0,$$

or
$$\cos 2\psi_1+\cos 2\psi_2+\cos 2(\psi_1+\psi_2)=-\tfrac{3}{2}.$$

If $\psi_1=\psi_2$, the expression reduces to

$$2\cos 2\psi_1+\cos 4\psi_1=-\tfrac{3}{2},$$

the solution of which gives

$$\cos 2\psi_1=-\tfrac{1}{2} \quad \text{or} \quad \psi_1=60°.$$

Thus again, the spacing of the armature coils must be symmetrical if harmonics are to be absent with symmetrical loading.

Generally, if the loadings and spacings are all equal, the condition becomes

$$n + 2(n-1)\cos 2\psi + (n-2)\cos 4\psi + (n-3)\cos 6\psi + \ldots + \cos 2(n-1)\psi = 0.$$

If ψ be put $= \frac{\pi}{n}$ the series within the bracket can be shown to be equal to $-\frac{1}{2}$ whether n is odd or even, thus satisfying the condition that the whole expression should be zero.

Thus the coils must not only be evenly spaced, but the spacing must be at the angular interval $\frac{\pi}{n}$ in order that when they are equally loaded there may be no further harmonics in the current curve beyond the fundamental.

It is clearly possible to state at any desired stage in the sequence of Lyle's or Pupin's series of equations the conditions necessary for the suppression of harmonics in the current curves beyond that stage.

CXXIX. *Notices respecting New Books.*

Surface Equilibria of Biological and Organic Colloids. By P. Lecomte Du Noüy, D.Sc. Amer. Chem. Soc. Monograph Series. (The Chemical Catalog Co. Inc., 19 East 24th Street, New York, U.S.A. 1926.)

IN this book the author uses physical methods with the object of throwing some light on certain biological problems. For this purpose he utilizes chiefly such physical properties as surface tension, interfacial tension, etc.

The measurements of these properties are difficult and troublesome, even when it is a question of comparatively simple physical phenomena.

Anybody experienced in the work on surface tension knows the difficulties due to some "unknown causes."

This branch of physics is not very advanced from either theoretical or experimental points of view, which makes work of this kind difficult. Such a state of affairs has resulted in a large quantity of purely empirical work of doubtful value. The existing figures obtained by various methods very often differ from one another within 8 per cent., and before any further progress can be made more accurate methods must come into general use.

For this reason the biological work in this book is preceded by a purely physical research, with the view of producing an accurate method of measuring the surface tension.

Chapter I discusses different experimental methods and points out which of them have to be preferred under various circumstances.

It gives a lot of valuable information with regard to accuracy of measurements and standardization of various conditions on which the accurate measurements depend. Thus, for example, it is useful to know exactly how to treat the glass in order to get always uniform results. It is shown how pedantically certain conditions have to be observed to secure the proper wetting of the glass by liquids. The same applies to the methods of preparing standard solutions. The author evolved an improved form of a tensiometer—an instrument permitting an accurate measurement of surface tension without much trouble, which will be of much use to all those who may want to experiment on these lines.

In Chapter 9 the author describes the same apparatus adapted for measurement of interfacial tension. Considering that the methods used by most of the experimentalists up to now were far from being accurate, the new precision instrument will be of use to physicists, as well as biologists, in view of the interest this subject presents for biological science. The author quite rightly omits the second decimal figure in his measurements as meaningless. Although the described apparatus permits of some accurate measurements of interfacial tension, the author's figures have no definite physical meaning, not only as far as decimal places are concerned, but even in their order of magnitude. On page 171 he says: "..... Quincke .... gave for the interfacial tension water-carbon bisulphide the value of 37·6 dynes, while we obtain 33·8 dynes and Harkins 54·09 dynes. The difference between the value given by Harkins and those of Quincke and ourselves is probably due to the fact that Harkins measures the value of the dynamic tension, while we measure the static value."

However, it can be shown that practically identical values can be obtained by both methods, if the system in question is in a state of equilibrium. In cases mentioned the figures were obtained without any reference to the state of equilibrium, without which they cannot have any definite meaning. See H. Freundlich, *Die Kapillarchemie*, Leipzig, 1922, p. 135. Sometimes it is not easy to attain the equilibrium, but it can be done all the same, in which case only one obtains definite figures. For this reason the figures on p. 172 for interfacial tension of water-carbon bisulphide and water-ethyl ether do not necessarily have a definite meaning, as the systems may be indefinitely distant from the state of equilibrium. Until the experiment is done in standard conditions, it is futile to speak about decimal places before the order of magnitude is established correctly.

So much about the measurements of surface tension and interfacial tension.

From the point of view of molecular physics Chapters 3 and 4 are of interest as throwing light on the molecular structure of matter. Some of the figures relating to molecular dimensions differ somewhat from those obtained by X-ray analysis, but the Avogadro constant N is in close agreement with the same obtained by other methods.

G. Antonoff.

CXXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 976.]

January 19th, 1927.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

THE following communications were read :—

1. 'The Geology of the Austral or Tubuai Islands (South Pacific).' By Lawrence John Chubb, M.Sc.

The Austral or Tubuai Group is situated about 350 miles south of Tahiti, and 1800 miles north-east of New Zealand. It includes seven islands, of which four are here described.

Rapa is a crateriform island, the slopes of which have been deeply dissected by radial streams, while the ends of the spurs between the valleys have been carved into precipitous cliffs by the sea. After one of the radial streams had captured the drainage of the crater, the island was submerged, with the result that the river-valleys were embayed and the crater flooded. Subsequently, slight elevation occurred. The formation of cliffs has proceeded so far that the greatest heights are now around the coast, while the subaërial erosion has resulted in the formation of aiguilles. Small coral-reefs are developed in the bays.

Marotiri, at the south-eastern extremity of the group, consists of a number of needle-like stacks rising out of the sea, and situated roughly on the circumference of a circle. Probably it represents the last stage of an island of the type of Rapa, which has subsided until all except the highest peaks are submerged.

Rurutu is without the sharp peaks and serrated ridges characteristic of Rapa, and the valley-mouths are not embayed. It is surrounded by an elevated coral-reef, rising to 200 or 300 feet above sea-level, which from its form appears to be of the fringing variety. This reef is unconformably related to the underlying rocks, and faces the sea in a line of vertical cliffs. At its summit there is a terrace behind which the hills of volcanic rock arise. Above a height of 600 feet these are deeply weathered to a red clay, and raised plateaux occur at different altitudes. The history of the island appears to be one of frequently-renewed, intermittent elevation, stationary periods being indicated by the raised plateaux, and the different degrees of weathering of the rocks at different levels. In the later stages a fringing-reef came into existence, which was finally uplifted. A narrow fringing-reef has developed around the island in recent times.

Rimatara is surrounded by a coral-reef about 2 miles wide. The outer edge of the central island is occupied by an elevated reef, which faces the sea in a line of cliffs 20 or 30 feet high.

The islands are arranged along lines having a general west-north-westerly and east-south-easterly trend, and it is suggested that the movements of elevation and subsidence which they have undergone may be due to the fact that they are situated on a submerged anticlinal fold, the crest of which has moved northwards.

2. 'The Petrography of the Austral or Tubuai Islands (Southern Pacific).' By Walter Campbell Smith, M.C., M.A., Sec.G.S., and Lawrence John Chubb, M.Sc.: with Chemical Analyses by Edgar Donald Mountain, M.A.

Except for a few small local occurrences of pyroclastic rocks, the volcanic rocks of Rapa consist of phonolitic and basaltic lavas invaded by many dykes and other small intrusions. Of the latter the most interesting probably forms the plug in the vent of the main volcano. It is an extremely melanocratic olivine-theralite, richer at the same time in nepheline or in olivine than any hitherto recorded. It bears fairly close relationship to Tyrrell's kylite from Benbeoch, Dalmellington, and should probably be included in Lacroix's group of luscladite. Other interesting intrusions are a crinanite, almost identical with that which forms the Dippin Sill in South-Eastern Arran, and a kylite.

The lavas and smaller dykes appear to form a single series:—trachytoid phonolite, trachybasalt, basic andesine-andesite, basic olivine-basalt, and basalt with abundant phenocrysts of augite and olivine. The basic porphyritic basalts are the predominant lavas: they resemble the picritic basalts of Hawaii and the ankaramites (ultrabasic basalts) of Tahiti. All the acid and basic lavas compare very closely with rocks from Tahiti, while rocks comparable with the trachybasalt and the basic andesine-andesite have been described from Hawaii.

In Rurutu occurs an olivine-bearing nepheline-tephrite, which resembles a rock described from Franklin Island (Antarctica). Otherwise the basic lavas found in this island are similar to those of Rapa.

Eight chemical analyses of the rocks are contributed by Mr. E. D. Mountain.

February 2nd.—Sir Arthur Smith Woodward, LL.D., F.R.S., Vice-President, in the Chair.

The following communication was read:—

'The Geology of the Naparima Region of Trinidad (British West Indies).' By Prof. Vincent Charles Illing, M.A., F.G.S.

The area around San Fernando (Trinidad) has long been regarded as the key to the geological history of Trinidad in Tertiary

times. It is covered almost entirely by a series of sands, clays, and marls of Lower and Middle Tertiary age, the marls being responsible for the black soils which have become the home of the sugar-cane industry.

The study of these Tertiary deposits has shown that they have been formed in two separate basins, separated by an important zone of uplift extending from San Fernando in an east-north-easterly direction. The deposits of the two basins had at some periods remarkably different facies, and it has been necessary to introduce two separate classifications. The succession in each basin, and particularly on the border-land, is interrupted by repeated unconformities showing overlap and overstep on to the old shore-line.

The Upper Argiline, generally considered to be Cretaceous, is placed in the Upper Eocene on the evidence of the foraminifera, and is followed unconformably by a series of sands and silts, also of Upper Eocene age. The Oligocene appears to be only in part represented, but the late Oligocene and early Miocene Periods show a thick series of clays, marls, and sands. The marl facies is almost completely restricted to the southern basin, and is considered to be merely a facies of the more widespread foraminiferal clays. It changes rapidly, both in thickness and in lithology, when traced northwards and southwards, but is more consistent along the strike.

The rocks of the area are moulded by a series of thrusting movements that come generally from the northward, the main trend of the folding being east-north-easterly. In Northern Naparima the soft Tertiary strata are crumpled, isoclinally folded, and overthrust. In the middle of the area the folding is still complicated, but is less intense and more irregular; while in the south the folds are open and more symmetrical.

Associated with the movements which have clearly recurred at distinct periods in Tertiary time, there has been emergence of the central land-ridge and the formation of shallow-water beach-deposits at the maximum phases of uplift. These deposits follow the main line of thrusting, and are themselves involved in the later thrusting movements.

February 23rd.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

The following communication was read:—

'The Geology of the Saltern Cove Area (Torbay).' By Leslie George Anniss, B.Sc.

The small complex of Lower, Middle, and Upper Devonian rocks which occurs at Saltern Cove, near Paignton, exhibits features of both tectonic and stratigraphical interest. The series here termed Red Shale Group (Upper Frasnian and Lower

Fammenian) are overthrust on the north by the Staddon Grit and Shales (Upper Coblentzian), and on the south by the 'Massive Limestone' (probably Lower Frasnian), which is brought into position by a thrust of low hade from the south-east. The 'Massive Limestone' forms the high ground on the south and also the summit of Sugar Loaf Hill, between which denudation has cut a deep valley exposing the Upper Devonian as a 'window.'

The present paper is mainly concerned with the Upper Devonian, which is a series of Red Shales, thin limestones, and tuffs. From these beds goniatites have been collected, which fix the fossiliferous horizon as Zone 1γ of Wedekind; while the still higher strata appear, from evidence given, to be the equivalent of the Cypridinen-Schiefer of the Eifel Area.

Several of the goniatites from this fossiliferous horizon are here recorded for the first time from Great Britain.

Associated with the Upper Devonian is a decomposed albite-dolerite, which contains iddingsite and quartz-hæmatite pseudomorphs after olivine; it is shown that this rock has no connexion with the intrusions of the Torquay and Dartmouth areas, but is comparable with those of the Ashprington and Totnes areas.

CXXXI. *Intelligence and Miscellaneous Articles.*

THE USE OF GASFILLED PHOTOELECTRIC CELLS.

BY N. R. CAMPBELL.

ON p. 1046 of the present volume, lines 3 and 4 from the bottom, it is stated that "the capacity....is reduced to a minimum." This is an error which might mislead seriously anybody trying to use the method. There is an optimum capacity for each cell, which may be as great as 100 cm.; accordingly a small variable condenser, such as is used in radio receiving sets, should be connected in parallel with the cell. The reason for this necessity has yet to be discovered.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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